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(54) Title: METHOD FOR MAKING FLUOROPOLYMERS CONTAINING ION EXCHANGE GROUPS

(57) Abstract: The invention pertains to a method of making fluoropolymers comprising ion exchange groups using certain polymeric derivatives including a plurality of ionic groups selected from the group consisting of $-SO_3X_a$ and $-COOX_a$, whereas X_a is H, an ammonium group or a monovalent metal. The invention further relates to fluoropolymer dispersions comprising the fluorinated polymer with ion exchange groups and the polymeric derivative including ionic groups.

Description

Method for making fluoropolymers containing ion exchange groups

Reference to related applications

This application claims priority from European patent application EP22159375.9 filed on March 1, 2022, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0001] The present invention relates to a method of making fluoropolymer dispersions using certain polyfunctional polymeric derivatives, and to the fluoropolymers obtained therefrom.

Background Art

[0002] Fluoropolymers, i.e. polymers having a fluorinated backbone, have been long known and have been used in a variety of applications because of several desirable properties such as heat resistance, chemical resistance, weatherability, UV-stability etc. Fluorinated polymers comprising ion exchange groups have been used for the manufacture of proton exchange membranes, for instance for use in fuel cell applications.

[0003] A frequently used method for producing fluoropolymers involves aqueous emulsion polymerization of one or more fluorinated monomers generally involving the use of fluorinated surfactants. Frequently used fluorinated surfactants include perfluorooctanoic acids and salts thereof, in particular ammonium perfluorooctanoic acid.

[0004] Recently, perfluoroalkanoic acids having 8 or more carbon atoms have raised environmental concerns. For instance, perfluoroalkanoic acids have been found to show bioaccumulation. Accordingly, efforts are now devoted to phasing out such compounds and methods have been developed to manufacture fluoropolymer products using alternative surfactants having a more favourable toxicological profile.

[0005] **EP 0341716** A (ASAHI GLASS CO LTD) 15/11/1989 is directed to a process for preparing an aqueous dispersion, which comprises subjecting a monomer to emulsion polymerization in an aqueous medium in the

presence of a fluorine-containing copolymer comprising units derived from a fluoroolefin, and units having a hydrophilic side chain having a group which maybe: (i) a carboxylic acid group or a carboxylate group of the formula -COOM, (ii) a sulfonic acid group or a sulfonate group of the formula -SO_3M and (iii) a phosphonic acid group or a phosphonate group of the formula -PO_3M (wherein M is hydrogen, an alkali metal, a quaternary ammonium group, or a quaternary phosphonium group), and (iv) an amido group, and having a number average molecular weight at a level of from 1000 to 500000, particularly from 3000 to 400000. The monomer being polymerised is a fluoroolefin having from 2 to 4 carbon atoms such as hexafluoropropylene, pentafluoropropylene, tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene or vinylidenefluoride, and a vinyl compound, an allyl compound, a fluorinated vinyl compound or a fluorinated allyl compound are preferred, since their polymerization gives rise to an aqueous dispersion capable of providing a coating layer having excellent weather resistance.

[0006] **WO 2012/082707 A1** (3M INNOVATIVE PROPERTIES COMPANY) discloses microemulsions obtained by mixing water, at least one ethylenically unsaturated fluoromonomer, and at least one oligomeric fluorosulfinic compound and/or at least one ethylenically unsaturated, polymerizable monomeric fluorosulfinic compounds and their use for polymerization of the at least one ethylenically unsaturated fluoromonomer. The oligomeric and the polymerisable monomeric fluorosulfinic compounds have low molecular weights and are characterised by the presence of sulfinic/sulfinate functional groups – SO_2M in which M is a cation.

[0007] **WO 2018/167190 A1** (SOLVAY SPECIALTY POLYMERS ITALY SpA) 28/09/2018 discloses a method for making a fluoropolymer comprising emulsion polymerizing one or more than one fluorinated monomer in an aqueous medium in the presence of at least one radical initiator and at least one polyfunctional dispersant:

- comprising a backbone chain comprising recurring units derived from one or more ethylenically unsaturated monomers,

- having a molecular weight and distribution thereof such that said dispersant is substantially free from fractions having molecular weight of less than 3000,
- comprising a plurality of ionic groups selected from the group consisting of $–SO_3X_a$, $-PO_3X_a$ and $–COOX_a$, whereas X_a is H, an ammonium group or a monovalent metal, in an amount of at least 1.75 meq/g, with respect to the weight of dispersant, wherein the said dispersant is used in an amount of 0.01% by weight and 5.00% by weight, based on the total weight of the aqueous medium. WO 2018/167190 A1 discloses in particular the preparation of PTFE in the presence of a dispersant (D) comprising $–SO_3X_a$ ionic groups.

[0008] It has been found that the use of certain polyfunctional dispersants disclosed in **WO 2018/167190 A1**, can be advantageously used in processes for the aqueous emulsion polymerization of monomers comprising hydrolysable groups to provide dispersions of polymers comprising hydrolysable groups free of surfactants.

Disclosure of Invention

[0009] A first object of the invention is a method for making a fluoropolymer comprising a plurality of hydrolysable groups [polymer (P)], said method comprising emulsion polymerising in an aqueous medium:

- tetrafluoroethylene, and
- at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group,

in the presence of at least one radical initiator and at least one polyfunctional dispersant [dispersant (D)], said dispersant (D):

- having a weight average molecular weight (M_w) of at least 15000 and at most 800000,
- comprising a backbone chain comprising recurring units deriving from one or more ethylenically unsaturated monomers, and
- comprising a plurality of ionic groups selected from the group consisting of $–SO_3X_a$ and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.

[0010] The Applicant has surprisingly found that dispersant (D), thanks to the presence of ionic groups as pendant groups in the fluorinated chain, despite its high molecular weight, possesses sufficient surface active effect and dispersing ability for ensuring efficient stabilization of the fluoropolymer in the aqueous polymerization environment.

[0011] Advantageously, dispersant (D) has a molecular weight and a molecular weight distribution such that it is substantially free from fractions having molecular weight of less than 3000.

[0012] The ionic groups in dispersant (D) are in an amount of at least 1.00 meq/g, with respect to the weight of dispersant (D).

[0013] The hydrolysable groups in polymer (P) are preferably selected from –SO_2X and –COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group.

[0014] Dispersant (D) is used in an amount from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.

[0015] In an advantageous embodiment of the invention, the ionic groups in dispersant (D) are obtainable from the hydrolysable groups of polymer (P) which is the product of the emulsion polymerisation process. In this embodiment, at the end of the polymerization process polymer (P) does not require any purification step to remove the residues of dispersant (D). Indeed the presence of dispersant (D) will not have any detrimental effect of the properties of polymer (P) thanks to the similar chemical nature.

[0016] In an even more advantageous embodiment of the invention, dispersant (D) has the same monomer composition as polymer (P) being obtained at the end of the process, the sole difference being the presence of ionic groups –SO_3X_a and –$COOX_a$ in place of hydrolysable groups –SO_2X and –COOZ, as defined above.

[0017] **Definitions**

[0018] The expression “fluorinated monomer” is hereby intended to denote an ethylenically unsaturated monomer comprising at least one fluorine atom.

[0019] The expression “essentially consisting of” when used in respect of a polymer composition, including dispersant (D), is meant to indicate that said polymer contains no more than 1 mol% , with respect to total moles of

recurring units of end-groups, impurities, defects and other spurious recurring units in addition to the listed recurring units.

[0020] **Polymer (P)**

[0021] The method of the invention comprises emulsion polymerizing in an aqueous medium tetrafluoroethylene and at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group. The hydrolysable group is selected from the group consisting of –SO_2X and –COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group.

[0022] Polymer (P) preferably comprises recurring units deriving from at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group -SO_2X wherein X is a halogen, hereinafter referred to as [monomer (A)].

[0023] Non limiting examples of suitable monomers (A) are selected from the group consisting of:

- sulfonyl halide fluoroolefins of formula: $CF_2=CF(CF_2)_pSO_2X$, with X being halogen, preferably F or Cl, more preferably F, wherein p is an integer between 0 and 10, preferably between 1 and 6, more preferably p is equal to 1, 2 or 3;
- sulfonyl halide fluorovinylethers of formula: $CF_2=CF\text{-}O\text{-}(CF_2)_mSO_2X$, with X being halogen, preferably F or Cl, more preferably F, wherein m is an integer between 1 and 10, preferably between 1 and 6, more preferably between 2 and 4, even more preferably m equals 2;
- sulfonyl halide fluoroalkoxyvinylethers of formula: $CF_2=CF\text{-}(OCF_2CF(R_{F1}))_w\text{-}O\text{-}CF_2(CF(R_{F2}))_ySO_2X$

with X being halogen, preferably F or Cl, more preferably F, wherein w is an integer between 0 and 2, R_{F1} and R_{F2}, equal or different from each other, are independently F, Cl or a $C_1\text{-}C_{10}$ fluoroalkyl group, optionally substituted with one or more ether oxygen atoms, y is an integer between 0 and 6; preferably w is 1, R_{F1} is $-CF_3$, y is 1 and R_{F2} is F;

- sulfonyl halide aromatic fluoroolefins of formula $CF_2=CF\text{-}Ar\text{-}SO_2X$ with X being halogen, preferably F or Cl, more preferably F, wherein Ar is a $C_5\text{-}C_{15}$ aromatic or heteroaromatic group.

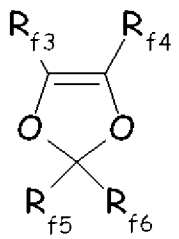
[0024] Preferably monomer (A) is selected from the group of the sulfonyl fluoride fluorovinylethers of formula CF_2=CF-O-$(CF_2)_m$-SO_2F, wherein m is an integer between 1 and 6, preferably between 2 and 4.

[0025] More preferably monomer (A) is CF_2=$CFOCF_2CF_2$-SO_2F (perfluoro-5-sulfonylfluoride-3-oxa-1-pentene).

[0026] Additional fluorinated monomers may be present during the polymerization process and incorporated in polymer (P).

[0027] Non limiting examples of suitable ethylenically unsaturated fluorinated monomers are:

- C_2-C_8 perfluoroolefins, such as hexafluoropropylene, perfluoroisobutylene;
- C_2-C_8 hydrogen-containing fluoroolefins, such as trifluoroethylene, vinylidene fluoride, vinyl fluoride, pentafluoropropylene, and hexafluoroisobutylene;
- C_2-C_8 chloro- and/or bromo- and/or iodo-containing fluoroolefins, such as chlorotrifluoroethylene and bromotrifluoroethylene;
- fluoroalkylvinylethers of formula CF_2=$CFOR_{f1}$, wherein R_{f1} is a C_1-C_6 fluoroalkyl, e.g. -CF_3, -C_2F_5, -C_3F_7;
- fluorooxyalkylvinylethers of formula CF_2=$CFOX_0$, wherein X_0 is a C_1-C_{12} fluorooxyalkyl group comprising one or more than one ethereal oxygen atom, including notably fluoromethoxyalkylvinylethers of formula CF_2=$CFOCF_2OR_{f2}$, with R_{f2} being a C_1-C_3 fluoro(oxy)alkyl group, such as -CF_2CF_3, -CF_2CF_2-O-CF_3 and –CF_3
- fluorodioxoles, of formula:



wherein each of R_{f3}, R_{f4}, R_{f5}, R_{f6}, equal or different each other, is independently a fluorine atom, a C_1-C_6 fluoro(halo)fluoroalkyl, optionally comprising one or more oxygen atom, e.g. -CF_3, -C_2F_5, -C_3F_7, -OCF_3, -$OCF_2CF_2OCF_3$.

[0028] Preferred fluorinated monomers for use in the method of the present invention, in addition to tetrafluoroethylene, include chlorotrifluoroethylene, hexafluoropropylene, vinyl fluoride, vinylidene fluoride.

[0029] Polymer (P) is preferably selected from polymers comprising or consisting essentially of:

- 50 to 99 mol%, preferably 50 to 98 mol%, even 5 to 95 mol%, with respect to total moles of polymer (P), of recurring units deriving from tetrafluoroethylene (TFE);
- 1 to 50 mol%, preferably 2 to 50 mol%, even 5 to 50 mol%, with respect to total moles of polymer (P), of recurring units deriving from at least one monomer selected from the group consisting of:

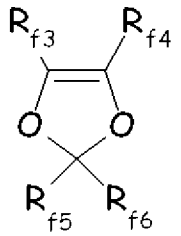
(j) sulfonyl halide fluorovinylethers of formula: $CF_2=CF-O-(CF_2)_mSO_2X$, with X being halogen, preferably F or Cl, more preferably F, wherein m is an integer between 1 and 10, preferably between 1 and 6, more preferably between 2 and 4, even more preferably m equals 2;

(jj) sulfonyl halide fluoroalkoxyvinylethers of formula: $CF_2=CF-(OCF_2CF(R_{F1}))_w-O-CF_2(CF(R_{F2}))_ySO_2X$ with X being halogen, preferably F or Cl, more preferably F, wherein w is an integer between 0 and 2, R_{F1} and R_{F2}, equal or different from each other, are independently F, Cl or a C_1-C_{10} fluoroalkyl group, optionally substituted with one or more ether oxygen atoms, y is an integer between 0 and 6; preferably w is 1, R_{F1} is $-CF_3$, y is 1 and R_{F2} is F; and

(jjj) mixtures thereof; and

- 0 to 45 mol%, preferably 0 to 40 mol%, even 0 to 25 mol%, with respect to total moles of polymer (P), of recurring units deriving from at least one hydrogenated and/or fluorinated monomer different from TFE, preferably a perfluorinated monomer, generally selected from the group consisting of hexafluoropropylene, perfluoroalkylvinylethers of formula $CF_2=CFOR'_{f1}$, wherein R'_{f1} is a C_1-C_6 perfluoroalkyl, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$; perfluoro-oxyalkylvinylethers of formula $CF_2=CFOR'_{O1}$, wherein R'_{O1} is a C_2-C_{12} perfluoro-oxyalkyl having one or more ether groups, including e.g. perfluoroalkyl-methoxy-vinylethers of formula $CF_2=CFOCF_2OR'_{f2}$ in which R'_{f2} is a C_1-C_6 perfluoroalkyl, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$ or a C_1-C_6 perfluorooxyalkyl having one or more ether groups, like $-C_2F_5-O-CF_3$;

fluorodioxoles, of formula:



wherein each of R_{f3}, R_{f4}, R_{f5}, R_{f6}, equal or different each other, is independently a fluorine atom, a C_1-C_6 fluoro(halo)fluoroalkyl, optionally comprising one or more oxygen atom, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-OCF_3$, $-OCF_2CF_2OCF_3$, preferably $-OCF_3$.

[0030] According to certain embodiments, polymer (P) comprises, consists essentially of, consists of:

(1) from 50 to 95 mol%, preferably from 55 to 93 mol% of recurring units deriving from TFE;

(2) from 5 to 50 mol%, preferably from 7 to 45 mol% of recurring units deriving from $–SO_2X$ groups-containing monomer (A), as above detailed;

(3) from 0 to 25 mol%, preferably from 0 to 20 mol% of recurring units deriving from fluorinated monomer(s) different from TFE, as above detailed.

[0031] Polymer (P) generally possess a weight average molecular weight (M_w), as measured by GPC with respect to polystyrene standards, using dimethylacetamide as eluent, of at least 50000, preferably of at least 85000 more preferably of at least 100000.

[0032] The weight average molecular weight (M_w), as measured by GPC with respect to polystyrene standards, using dimethylacetamide as eluent, of polymer (P) is generally of at most 700000, preferably at most 600000, more preferably at most 500000. Suitable ranges for most applications of polymer (P) are for instance from 150000 to 600000, preferably from 180000 to 500000.

[0033] Preferably polymer (P) has a number average molecular weight of at least 50000, preferably of at least 90000 and/or advantageously of at most 500000, preferably of at most 450000, as measured by GPC with respect

to polystyrene standards, using dimethylacetamide as eluent. The GPC method is detailed in the experimental section.

[0034] **Dispersant (D)**

[0035] Polyfunctional dispersant (D) comprises a backbone chain comprising recurring units deriving from one or more ethylenically unsaturated monomers, and a plurality of ionic groups selected from the group consisting of $–SO_3X_a$ and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal. Dispersant (D) does not contain unsaturated carbon-carbon bonds.

[0001] Dispersant (D) is used in an amount from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.

[0036] The amount of dispersant (D) in the emulsion polymerization process is of at least 0.05 wt %, preferably of at least 0.10 wt % and advantageously at most 4.00 wt %, preferably at most 3.50 wt %, even more preferably at most 3.00 wt % with respect to the total weight of the aqueous medium. A practical range is between 0.10 wt %and 2.75 wt %, preferably between 0.25 wt %and 2.00 wt %, even between 0.50 wt %and 1.75 wt % with respect to the total weight of the aqueous medium. In certain embodiments dispersant (D) is present in an amount between 0.25 wt %and 1.50 wt % with respect to the total weight of the aqueous medium.

[0037] While the polymerization is generally initiated in the presence of dispersant (D), it is not excluded to add further dispersant (D) during the polymerization, although such will generally not be necessary.

[0038] Dispersant (D) has a weight average molecular weight (M_w), as measured by GPC with respect to polystyrene standards, using dimethylacetamide as eluent, of at least 15000. The GPC method is detailed in the experimental section.

[0039] Upper boundaries for the weight average molecular weight (M_w), as measured by GPC with respect to polystyrene standards, using dimethylacetamide as eluent, of dispersant (D) are not particularly critical, provided the dispersant (D) possesses an amount of ionic groups per weight of dispersant which enable it to have adequate dispersability.

[0040] It is nonetheless understood that a practical range for the weight average molecular weight of dispersant (D) is generally of at most 800000, at most 600000, preferably at most 500000, more preferably at most 400000.

[0041] Preferably dispersant (D) has a weight average molecular weight of at least 20000, preferably of at least 25000, advantageously of at least 50000, at least 100000 or even at least 150000.

[0042] Particularly good results have been obtained with dispersants having a weight average molecular weight of from 50000 to 400000, even 150000 to 400000.

[0043] Dispersant (D) may advantageously have a number average molecular weight (M_n) of 7000 to 500000, preferably from 25000 to 400000, even from 50000 to 250000.

[0044] Advantageously, dispersant (D) is a polymer having a molecular weight and a molecular weight distribution such that dispersant (D) is substantially free from fractions having molecular weight of less than 3000.

[0045] Determination of substantial absence of fractions having molecular weight of less than 3000 can be done using GPC technique, with respect to polystyrene standards, using dimethylacetamide as eluent. The GPC method is detailed in the experimental section.

[0046] The expression “substantially free” in connection with dispersant (D) and fractions having molecular weight of less than 3000 is intended to mean that said fractions are present in an amount of at most 0.03 wt%, preferably at most 0.01 wt% and more preferably they are not detectable via GPC technique, as detailed above.

[0047] Dispersant (D) comprises a plurality of ionic groups selected from the group consisting of $–SO_3X_a$ and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal. The monovalent metal is typically selected from the group of the alkali metals, preferably it is sodium or potassium.

[0048] Preferably dispersant (D) comprises a plurality of ionic groups selected from the group consisting of $–SO_3X_a$ wherein X_a is selected from H, an ammonium group or a monovalent metal.

[0049] The amount of said ionic groups in dispersant (D) is generally of at least 1.00 meq/g, at least 1.10 meq/g, preferably at least 1.20 meq/g, more preferably at least 1.30 meq/g, with respect to the weight of dispersant (D).

Dispersants (D) which possess an amount of ionic group of less than 1.00 meq/g are believed to lack a sufficient polarity for solubilizing in the water phase and producing a stabilizing/surfactant-like effect. There's no substantial limitation as per the maximum amount of the said ionic groups in dispersant (D). It is generally understood that the said ionic groups are generally present in an amount of at most 2.50 meq/g, preferably at most 2.20 meq/g, more preferably at most 2.00 meq/g.

[0050] Dispersant (D) comprises said ionic groups as pendant groups covalently bound to recurring units deriving from an ethylenically unsaturated functional monomer [monomer (X)].

[0051] Dispersant (D) may consist essentially of recurring units deriving from one or more than one monomer (X) or it can be a copolymer comprising recurring units deriving from one or more than one monomer (X) and recurring units deriving from one or more than one additional monomer different from monomer (X).

[0052] Generally, monomer (X) is a fluorinated monomer; one or more than one additional monomer different from monomer (X) may be a fluorinated monomer.

[0053] According to certain embodiments of the invention, dispersant (D) is polymer comprising a plurality of $–SO_3X_a$ groups.

[0054] Dispersant (D) may consist essentially of recurring units deriving from one or more than one ethylenically unsaturated monomer comprising a $–SO_3X_a$ group. Alternatively, dispersant (D) may comprise recurring units deriving from one or more than one monomer comprising a $–SO_3X_a$ group and recurring units deriving from one or more than one monomer which does not contain a $–SO_3X_a$ group.

[0055] The expression "recurring units deriving from" in connection with a monomer comprising a $–SO_3X_a$ group is intended to encompass both i) recurring units as derived/directly obtained from polymerizing said monomer and ii) recurring units derived/obtained from polymerizing a monomer comprising a functional group precursor to a $–SO_3X_a$ group followed by modification and/or post-treatment of the polymer, e.g. by hydrolysis. In other terms a dispersant comprising recurring units deriving from one or more than one monomer comprising a $–SO_3X_a$ group, may be

obtained by polymerizing monomers comprising $–SO_2X$ groups followed by hydrolysis of the same. For the avoidance of doubt dispersant (D) contains ionic $–SO_3X_a$ groups.

[0056] Suitable dispersants (D) comprising a plurality of $–SO_3X_a$ group are polymers comprising recurring units deriving from:

- at least one ethylenically unsaturated fluorinated monomer containing at least one $-SO_2X$ group, with X being a halogen (eg. F) or $–OX_a$, with X_a is H, an ammonium group or a monovalent metal; and
- recurring units deriving from at least one ethylenically unsaturated fluorinated monomer free from $-SO_2X$ group, [monomer (B)] hereinafter.

[0057] Ethylenically unsaturated fluorinated monomers containing at least one $-SO_2X$ group suitable for the preparation of dispersant (D) can be selected from the list consisting of monomer (A) detailed above, wherein X is a halogen (eg. F) or $–OX_a$, with X_a = H, an ammonium group or a monovalent metal.

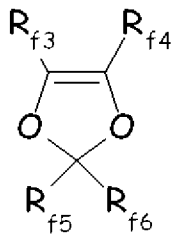
[0058] The phrase “at least one monomer” is used herein with reference to monomers of both type (A) and (B) to indicate that one or more than one monomer of each type can be present in the dispersant (D). Hereinafter the term monomer will be used to refer to both one and more than one monomer of a given type.

[0059] Non limiting examples of suitable ethylenically unsaturated fluorinated monomers of type (B) are:

- C_2-C_8 perfluoroolefins, such as tetrafluoroethylene, hexafluoropropylene, perfluoroisobutylene;
- C_2-C_8 hydrogen-containing fluoroolefins, such as trifluoroethylene, vinylidene fluoride, vinyl fluoride, pentafluoropropylene, and hexafluoroisobutylene;
- C_2-C_8 chloro- and/or bromo- and/or iodo-containing fluoroolefins, such as chlorotrifluoroethylene and bromotrifluoroethylene;
- fluoroalkylvinylethers of formula $CF_2=CFOR_{f1}$, wherein R_{f1} is a C_1-C_6 fluoroalkyl, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$;
- fluorooxyalkylvinylethers of formula $CF_2=CFOX_0$, wherein X_0 is a C_1-C_{12} fluorooxyalkyl group comprising one or more than one ethereal oxygen

atom, including notably fluoromethoxyalkylvinylethers of formula $CF_2=CFOCF_2OR_{f2}$, with R_{f2} being a C_1-C_3 fluoro(oxy)alkyl group, such as $–CF_2CF_3$, $-CF_2CF_2-O-CF_3$ and $–CF_3$

- fluorodioxoles, of formula:



wherein each of R_{f3}, R_{f4}, R_{f5}, R_{f6}, equal or different each other, is independently a fluorine atom, a C_1-C_6 fluoro(halo)fluoroalkyl, optionally comprising one or more oxygen atom, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-OCF_3$, $-OCF_2CF_2OCF_3$.

[0060] Preferably monomer (B) is selected among:

- C_2-C_8 perfluoroolefins selected from tetrafluoroethylene and/or hexafluoropropylene;
- C_2-C_8 hydrogen-containing fluoroolefins, selected from trifluoroethylene, vinylidene fluoride, and vinyl fluoride; and
- mixtures thereof.

[0061] More preferably monomer (B) is tetrafluoroethylene.

[0062] In a preferred embodiment dispersant (D) is a fluorinated polymer comprising a plurality of $–SO_3X_a$ functional groups, and consisting essentially of, consisting of, recurring units deriving from at least one ethylenically unsaturated fluorinated monomer containing at least one $–SO_3X_a$ group and from at least one ethylenically unsaturated fluorinated monomer (B).

[0063] According to certain embodiments, at least one monomer (B) of the dispersant (D) is TFE.

[0064] Preferred dispersants (D) are selected from the group consisting of polymers comprising, essentially consisting of:

- 50 to 99 mol%, preferably 50 to 98 mol%, even 50 to 95 mol%, with respect to total moles of dispersant (D), of recurring units deriving from tetrafluoroethylene (TFE);

- 1 to 50 mol%, preferably 2 to 50 mol%, even 5 to 50 mol%, with respect to total moles of dispersant (D), of recurring units deriving from at least one monomer selected from the group consisting of:

(j) sulfonyl halide fluorovinylethers of formula: $CF_2=CF-O-(CF_2)_mSO_2X$, with X being OX_a, with X_a as above detailed or X is halogen, preferably F or Cl, more preferably F, wherein m is an integer between 1 and 10, preferably between 1 and 6, more preferably between 2 and 4, even more preferably m equals 2;

(jj) sulfonyl halide fluoroalkoxyvinylethers of formula: $CF_2=CF-(OCF_2CF(R_{F1}))_w-O-CF_2(CF(R_{F2}))_ySO_2X$

with X being OX_a, with X_a as above detailed or X is halogen, preferably F or Cl, more preferably F, wherein w is an integer between 0 and 2, R_{F1} and R_{F2}, equal or different from each other, are independently F, Cl or a C_1-C_{10} fluoroalkyl group, optionally substituted with one or more ether oxygen atoms, y is an integer between 0 and 6; preferably w is 1, R_{F1} is $-CF_3$, y is 1 and R_{F2} is F; and

(jjj) mixtures thereof; and

- 0 to 45 mol%, preferably 0 to 40 mol%, even 0 to 25 mol%, with respect to total moles of dispersant (D), of recurring units deriving from at least one hydrogenated and/or fluorinated monomer different from TFE, preferably a perfluorinated monomer, generally selected from the group consisting of hexafluoropropylene, perfluoroalkylvinylethers of formula $CF_2=CFOR'_{f1}$, wherein R'_{f1} is a C_1-C_6 perfluoroalkyl, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$; perfluoro-oxyalkylvinylethers of formula $CF_2=CFOR'_{O1}$, wherein R'_{O1} is a C_2-C_{12} perfluoro-oxyalkyl having one or more ether groups, including e.g. perfluoroalkyl-methoxy-vinylethers of formula $CF_2=CFOCF_2OR'_{f2}$ in which R'_{f2} is a C_1-C_6 perfluoroalkyl, e.g. $-CF_3$, $-C_2F_5$, $-C_3F_7$ or a C_1-C_6 perfluorooxyalkyl having one or more ether groups, like $-C_2F_5-O-CF_3$.

[0065] According to certain embodiments, the preferred dispersant (D) comprises, essentially consists of:

- from 50 to 95 mol%, preferably from 55 to 93 mol% of recurring units deriving from TFE;

- from 5 to 50 mol%, preferably from 7 to 45 mol% of recurring units deriving from $–SO_2X$ groups-containing monomer(s), monomer (A);

- from 0 to 25 mol%, preferably from 0 to 20 mol% of recurring units deriving from fluorinated monomer(s) different from TFE, monomer (B).

[0066] In an advantageous embodiment of the invention both polymer (P) and dispersant (D) comprise:

- from 50 to 95 mol%, preferably from 55 to 93 mol% of recurring units deriving from TFE;
- from 5 to 50 mol%, preferably from 7 to 45 mol% of recurring units deriving from $–SO_2X$ groups-containing monomer(s), monomer (A);
- from 0 to 25 mol%, preferably from 0 to 20 mol% of recurring units deriving from fluorinated monomer(s) different from TFE, monomer (B).

[0067] In certain embodiments of the invention, dispersant (D) has the same molar composition as polymer (P).

[0068] In a very advantageous embodiment of the invention, polymer (P), after hydrolysis of the hydrolysable groups, is used as dispersant in a further polymerization process.

[0069] Hence the method of the invention comprises the step of: recovering polymer (P), hydrolysing the hydrolysable $–SO_2X$ groups to obtain $–SO_3X_a$ groups to obtain dispersant (D).

[0070] The inventive method thus comprises the step of preparing dispersant (D) by emulsion polymerising in an aqueous medium:

- tetrafluoroethylene, and
- at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group selected from $-SO_2X$ and -COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group,

in the presence of at least one radical initiator and a dispersant [dispersant (Dx)] to obtain a polymer comprising a plurality of hydrolysable groups; hydrolysing the hydrolysable groups to obtain corresponding ionic groups– SO_3X_a and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.

[0071] Dispersant (Dx) is present in an amount from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.

[0072] Dispersant (D) may be any dispersant know in the art for preparing fluoropolymers. Advantageously, dispersant (Dx) is dispersant (D).

[0073] Hence, in an advantageous embodiment, the inventive method comprises the step of preparing dispersant (D) by emulsion polymerising in an aqueous medium:

- tetrafluoroethylene, and
- at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group selected from $-SO_2X$ and -COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group,

in the presence of at least one radical initiator and a dispersant (Dx) having a weight average molecular weight from 15000 to 800000, comprising a backbone chain comprising recurring units deriving from one or more ethylenically unsaturated monomers, and comprising a plurality of ionic groups selected from the group consisting of $–SO_3X_a$ and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal;
to obtain a polymer comprising a plurality of hydrolysable groups;
hydrolysing the hydrolysable groups to obtain corresponding ionic groups– SO_3X_a and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.

[0074] Dispersant (Dx) has a molecular weight and a molecular weight distribution such that it is substantially free from fractions having molecular weight of less than 3000, as measured by GPC with respect to polystyrene standards, using dimethylacetamide as eluent. The GPC method is detailed in the experimental section.

[0075] The ionic groups in dispersant (Dx) are in an amount of at least 1.00 meq/g, with respect to the weight of dispersant (Dx).

[0076] Dispersant (Dx) is present in the emulsion polymerisation medium in an amount from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.

[0077] Dispersant (Dx) has the same monomer composition, average molecular weight and molecular weight distribution as dispersant (D) obtained at the end of the process.

[0078] Dispersant (D) as well as polymer (P) may be prepared by any polymerization process known in the art. Suitable processes for the preparation of such polymers are for instance those described in **US**

4940525 (THE DOW CHEMICAL COMPANY) 10/07/1990 , **EP 1323751** A (SOLVAY SOLEXIS SPA) 2/07/2003 , **EP 1172382** A (SOLVAY SOLEXIS SPA) 16/11/2002.

[0079] The aqueous emulsion polymerization may be carried out at a temperature between 10°C to 150°C, preferably 20°C to 130°C and the pressure is typically between 2 and 60 bar, in particular 5 to 45 bar.

[0080] The reaction temperature may be varied during the polymerization e.g. for influencing the molecular weight distribution, i.e., to obtain a broad molecular weight distribution or to obtain a bimodal or multimodal molecular weight distribution.

[0081] The pH of the polymerization media may be in the range of pH 1-10, preferably 2-10.

[0082] As said, the method of the invention is carried out in an aqueous medium in the presence of at least one radical initiator, i.e. any of the initiators known for initiating a free radical polymerization of ethylenically unsaturated monomers. Suitable radical initiators include notably peroxides and azo compounds and redox based initiators. Specific examples of peroxide initiators include, hydrogen peroxide, sodium or barium peroxide, diacylperoxides such as diacetylperoxide, disuccinyl peroxide, dipropionylperoxide, dibutyrylperoxide, dibenzoylperoxide, di-ter-butyl-peroxide, benzoylacetylperoxide, diglutaric acid peroxide and dilaurylperoxide, and further per-acids and salts thereof such as e.g. ammonium, sodium or potassium salts. Examples of per-acids include peracetic acid. Esters of the peracid can be used as well and examples thereof include tert.-butylperoxyacetate and tert.-butylperoxypivalate. Examples of inorganic initiators include for example ammonium-, alkali- or earth alkali- salts of persulfates, permanganic or manganic acid or manganic acids. A persulfate initiator, e.g. ammonium persulfate (APS), can be used on its own or may be used in combination with a reducing agent. Suitable reducing agents include bisulfites such as for example ammonium bisulfite or sodium metabisulfite, thiosulfates such as for example ammonium, potassium or sodium thiosulfate, hydrazines, azodicarboxylates and azodicarboxyldiamide (ADA). Further reducing agents that may be used include hydroxymethane sodium sulfinate

(Rongalite) or fluoroalkyl sulfinates such as those disclosed in **US 5285002** . The reducing agent typically reduces the half-life time of the persulfate initiator. Additionally, a metal salt catalyst such as for example copper, iron or silver salts may be added.

[0083] The amount of initiator may be between 0.01% by weight (based on the fluoropolymer to be produced) and 1.00% by weight. Still, the amount of initiator is preferably between 0.05 and 0.50% by weight and more preferably between 0.05 and 0.30% by weight, based on the fluoropolymer to be produced.

[0084] The aqueous emulsion polymerization can be carried out in the presence of other materials, such as notably paraffin waxes, buffers and, if desired, complex-formers or chain-transfer agents.

[0085] Examples of chain transfer agents that can be used include dimethyl ether, methyl t-butyl ether, alkanes having 1 to 5 carbon atoms such as ethane, propane and n-pentane, halogenated hydrocarbons such as CCl_4, $CHCl_3$ and CH_2Cl_2 and hydrofluorocarbon compounds such as $CH_2F\text{-}CF_3$ (R134a). Additionally esters like ethylacetate, malonic esters can be effective as chain transfer agent in the method of the invention.

[0086] Further, the aqueous emulsion polymerization of the method of the invention can be carried out in the presence of certain fluorinated fluids deprived of ionic groups, typically enabling formation of nanosized droplets (average size of less than 50 nm, preferably of less than 30 nm), and advantageously stabilized in aqueous dispersion by the presence of the dispersant (D).

[0087] Should the method of the invention be carried out in the presence of a fluorinated fluid, as above detailed, it may be preferable to first homogenously mix the dispersant (D) and said fluid in an aqueous medium, and then feeding the so obtained aqueous mixture of the dispersant (D) and said fluid in the polymerization medium. This technique is particularly advantageous as this pre-mix can advantageously enable manufacture of an emulsion of said fluid in an aqueous phase comprising the dispersant (D), wherein this emulsion comprises dispersed droplets of said fluid having an average size of preferably less than 50 nm, more preferably of less than 40 nm, even more preferably of less than 30 nm.

[0088] Fluids which can be used according to this embodiment are preferably (per)fluoropolyethers comprising recurring units (R1), said recurring units comprising at least one ether linkage in the main chain and at least one fluorine atom (fluoropolyoxyalkene chain). Preferably the recurring units R1 of the (per)fluoropolyether are selected from the group consisting of :

(I) –CFX-O-, wherein X is –F or $–CF_3$; and

(II) $–CF_2$-CFX-O-, wherein X is –F or $–CF_3$; and

(III) $–CF_2$-CF_2-CF_2-O-; and

(IV) $–CF_2$-CF_2-CF_2-CF_2-O-; and

(V) $–(CF_2)_j$-CFZ-O- wherein j is an integer chosen from 0 and 1 and Z is a fluoropolyoxyalkene chain comprising from 1 to 10 recurring units chosen among the classes (I) to (IV) here above; and mixtures thereof.

[0089] Should the (per)fluoropolyether comprise recurring units R1 of different types, advantageously said recurring units are randomly distributed along the fluoropolyoxyalkene chain.

[0090] Preferably the (per)fluoropolyether is a compound complying with formula (I-p) here below :

T_1-$(CFX)_p$-O-R_f-$(CFX)_{p'}$-T_2 (I-p)

wherein :

- each of X is independently F or CF_3;
- p and p', equal or different each other, are integers from 0 to 3;
- R_f is a fluoropolyoxyalkene chain comprising repeating units R°, said repeating units being chosen among the group consisting of :

(i) -CFXO-, wherein X is F or CF_3,

(ii) $-CF_2CFXO$-, wherein X is F or CF_3,

(iii) $-CF_2CF_2CF_2O$-,

(iv) $-CF_2CF_2CF_2CF_2O$-,

(v) $–(CF_2)_j$-CFZ-O- wherein j is an integer chosen from 0 and 1 and Z is a group of general formula $–OR_f'T_3$, wherein R_f' is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : -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_3 is a C_1 – C_3 perfluoroalkyl group, and mixtures thereof;

- T_1 and T_2, the same or different each other, are H, halogen atoms, C_1 – C_3 fluoroalkyl groups, optionally comprising one or more H or halogen atoms different from fluorine.

[0091] Generally speaking, the method of the invention is carried out in the substantial absence of fluorinated emulsifiers having a molecular weight of less than 1000.

[0092] The expression “substantial absence” when used in connection to the fluorinated emulsifiers means that no surfactant is purposely added to the polymerization. While impurities possibly qualifying as fluorinated surfactants with a molecular weight of less than 1000 might be tolerated, their amount is generally below of detection limit of standard analytical techniques (< 1 ppm, with respect to the aqueous medium).

[0093] More generally, the method of the invention is carried out in the substantial absence of fluorinated emulsifiers having a molecular weight of less than 3000.

[0094] More specifically, the method of the invention include polymerizing in an aqueous medium which is substantially free from fluorinated emulsifier [surfactant (FS)] of formula :

$R_{f§} (X^-)_j (M^+)_j$

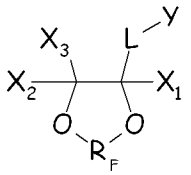
wherein $R_{f§}$ is a C_3 –C_{30} (per)fluoroalkyl chain, (per)fluoro(poly)oxyalkylenic chain, X^- is $-COO^-$, $-PO_3^-$ or $-SO_3^-$, M^+ is selected from H^+, NH_4^+, an alkaline metal ion and j can be 1 or 2 can be used.

[0095] As non-limitative examples of surfactants (FS), mention may be made of ammonium and/or sodium (per)fluoro(oxy)carboxylates, and/or (per)fluoropolyoxyalkylenes having one or more carboxylic end groups.

[0096] Examples of fluorinated surfactants , in particular of (per)fluorooxyalkylenic surfactants, are notably described in **US 2007015864** (3M INNOVATIVE PROPERTIES) 8/01/2007 , **US 2007015865** (3M INNOVATIVE PROPERTIES CO) 18/01/2007 , **US 2007015866** (3M INNOVATIVE PROPERTIES CO) 18/01/2007 , **US 2007025902** (3M INNOVATIVE PROPERTIES CO) 1/02/2007 .

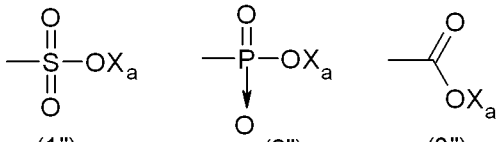
[0097] For instance, the fluorinated emulsifiers [surfactant (FS)] substantially excluded from the method of the invention are notably:

- $CF_3(CF_2)_{n1}COOM'$, in which n_1 is an integer ranging from 4 to 10, preferably from 5 to 7, and more preferably being equal to 6 ; M' represents H, NH_4, Na, Li or K, preferably NH_4 ;
- $T(C_3F_6O)_{n0}(CFXO)_{m0}CF_2COOM''$, in which T represents Cl or a perfluoroalkoxyde group of formula $C_kF_{2k+1}O$ with k is an integer from 1 to 3, one F atom being optionally substituted by a Cl atom ; n_0 is an integer ranging from 1 to 6 ; m_0 is an integer ranging from 0 to 6 ; M'' represents H, NH_4, Na, Li or K ; X represents F or CF_3 ;
- $F-(CF_2CF_2)_{n2}-CH_2-CH_2-RO_3M'''$, in which R is P or S, preferably S, M''' represents H, NH_4, Na, Li or K, preferably H ; n_2 is an integer ranging from 2 to 5, preferably n_2=3 ;
- $A-R_f-B$ bifunctional fluorinated surfactants, in which A and B, equal to or different from each other, are $-(O)_pCFX-COOM^*$; M* represents H, NH_4, Na, Li or K, preferably M* represents NH_4 ; X = F or CF_3 ; p is an integer equal to 0 or 1; R_f is a linear or branched perfluoroalkyl chain, or a (per)fluoropolyether chain such that the number average molecular weight of $A-R_f-B$ is in the range 300 to 1,000;
- $R'_f-O-(CF_2)_r-O-L-COOM'$, wherein R'_f is a linear or branched perfluoroalkyl chain, optionally comprising catenary oxygen atoms, M' is H, NH_4, Na, Li or K, preferably M' represents NH_4 ; r is 1 to 3; L is a bivalent fluorinated bridging group, preferably $–CF_2CF_2-$ or –CFX-, X = F or CF_3 ;
- $R''_f-(OCF_2)_u-O-(CF_2)_v-COOM''$, wherein R''_f is a linear or branched perfluoroalkyl chain, optionally comprising catenary oxygen atoms, M'' is H, NH_4, Na, Li or K, preferably M'' represents NH_4 ; u and v are integers from 1 to 3;
- $R'''_f-(O)_t-CHQ-L-COOM'''$, wherein R'''_f is a linear or branched perfluoroalkyl chain, optionally comprising catenary oxygen atoms, Q = F or CF_3, t is 0 or 1, M''' is H, NH_4, Na, Li or K, preferably M''' is NH_4; L is a bivalent fluorinated bridging group, preferably $–CF_2CF_2-$ or –CFX-, X = F or CF_3;
- cyclic fluorocompound of the following formula (I):



(I)

wherein X_1, X_2, X_3, equal or different from each other are independently selected among H, F, and C_{1-6} (per)fluoroalkyl groups, optionally comprising one or more catenary or non-catenary oxygen atoms; L represents a bond or a divalent group; R_F is a divalent fluorinated C_{1-3} bridging group; Y is a hydrophilic function selected from groups of formulae:



(1") (2") (3")

wherein X_a is H, a monovalent metal (preferably an alkaline metal) or an ammonium group of formula $-N(R'_n)_4$, wherein R'_n, equal or different at each occurrence, represents a hydrogen atom or a C_{1-6} hydrocarbon group.

[0098] The method of the invention typically results in an aqueous dispersion of the fluoropolymer further comprising dispersant (D), as above detailed.

[0099] The particle size (volume average diameter) of the fluoropolymer is typically between 40 nm and 400 nm with a typical particle size between 60 nm and about 350 nm being preferred.

[00100] The fluoropolymer may be isolated from the dispersion by coagulation or any other suitable technique if a polymer in solid form is desired.

[00101] Advantageously, the present invention may further comprise steps for obtaining polymer (P) in its ionic form as a powdery material [material (PP)] composed of a plurality of particles of at least one polymer comprising a plurality of ionic groups selected from the group consisting of $-SO_3X_a$ and $-COOX_a$, wherein X_a is H, an ammonium group or a metal, preferably a monovalent metal, said method comprising:

(1) providing an aqueous dispersion comprising particles of polymer (P) comprising a plurality of hydrolysable groups selected from the group

consisting of $-SO_2X_X$ and $-COOX_y$, wherein X_x is a halogen, in particular F or Cl and X_y is a C1-C4 alkoxy group; and

(2) contacting said aqueous dispersion with a basic hydrolysing agent to at least partially convert said groups $-SO_2X_X$ and $-COOX_y$ into corresponding groups $-SO_3X_b$ and $-COOX_b$, wherein X_b is an ammonium group or a monovalent metal, without causing any significant coagulation, so as to obtain an aqueous dispersion of particles of polymer (P) in ionic form; optionally

(3) contacting the dispersion obtained at the end of step (2) with at least one ion exchange resin, so as to at least partially remove residues of basic hydrolysing agent and/or other contaminants; and

(4) spray drying the dispersion obtained at the end of step (2) and optionally step (3) so as to obtain material (PP).

[00102] The at least one ion exchange resin in step (3) may be an anion exchange resin, a cation exchange resin or both.

[00103] When X_a is H, the process comprises a step in which cations X_b are exchanged with cations H^+. The ion exchange may be performed using a cation exchange resin in step (3) or by any other known mean, such as electrodialysis on bipolar membranes.

[00104] A process for the recovery of polymer (P) as a powder from an emulsion polymerization latex is described in WO2020/094563A1, the content of which is incorporated herein by reference.

[00105] The process for obtaining material (PP) may comprise further steps for the purification on the dispersion. Examples of suitable techniques comprise dialysis, electrodialysis and ultrafiltration. Said further purification step may be performed at any stage, typically between steps (2) and (4). When the optional step (3) is present, the further purification step is performed between steps (2) and (3) or, preferably, between steps (3) and (4).

[00106] Additional processes for the recovery of polymer (P) as a powder from the emulsion polymerization latex are for instance disclosed in WO22224105A1, the content of which is incorporated herein by reference.

[00107] Depending on the requirements of the application in which the fluoropolymer is to be used, the fluoropolymer in powder form may be

post-fluorinated so as to convert any chemically unstable end groups into stable -CF_3 end groups.

[00108] For coating applications, an aqueous dispersion of the fluoropolymer is desired and hence the fluoropolymer will not need to be separated or coagulated from the dispersion. To obtain a fluoropolymer dispersion suitable for use in coating applications such as for example in the impregnation of fabrics or other porous supports, it will generally be desired to add further stabilizing surfactants and/or to further increase the fluoropolymer solids. For example, non-ionic stabilizing surfactants may be added to the fluoropolymer dispersion.

[00109] The amount of fluoropolymer solids in the dispersion may be increased as needed or desired to an amount between 30 and 70 wt%. Any of the known concentration techniques may be used including ultrafiltration and thermal concentration.

[00110] In a preferred embodiment of the invention polymer (P) is used in the preparation of membranes for use in polymer electrolyte membrane fuel cells.

[00111] 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.

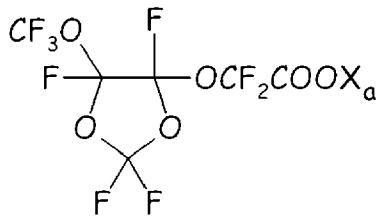
[00112] The invention will be now explained in more detail with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

[00113] **Preparative Example 1 – Preparation of Dispersant (D-1) by polymerization of tetrafluoroethylene (TFE) and perfluoro-5-sulfonylfluoride-3-oxa-1-pentene (SFVE) and successive hydrolysis**

[00114] **Step 1 – Polymerization**

[00115] In a 5 L autoclave the following reagents were charged:

- 1.8 L of demineralized water;
- 533 g of the monomer with formula: CF_2=CF-O-CF_2CF_2-SO_2F (SFVE);
- 89 g of a 46 wt% aqueous solution of the ammonium salt of the fluorocompound of formula:



with Xa being NH_4.

The autoclave, stirred at 650 rpm, was heated at 58°C. A water based solution with 16 g/L of ammonium persulfate was added in a quantity of 90 mL. The pressure was maintained at a value of 8.5 bar (abs.) by 8.2 bar of feeding tetrafluoroethylene (TFE). After the initial addition of 83 g, SFVE was added portionwise (23 g) each 5 wt% of TFE converted. The reaction was stopped after 200 min by stopping the stirring, cooling the autoclave and reducing the pressure by venting the TFE; a total of 340 g of TFE was fed into the autoclave. Overall, 0.12 grams of surfactant for each gram of converted TFE were used.

The latex thus obtained was degassed for 48 h with air flow to remove monomer's residuals and then coagulated through freeze-thawing. The powder was washed with deionized water (4 x 1L) for 30 min and dried in a vent oven at 120°C overnight.

A copolymer was obtained, said copolymer having an equivalent weight (EW) of 720 g/mol and possessing the following composition: TFE: 81.5 mol%; SFVE: 18.5 mol% as determined by FT-IR measurements. The The polymer had a number average molecular weight (M_n) of 93000 and a weight average molecular weight (M_w) of 241000. Substantially no fraction having a molecular weight below 3000 was detected by GPC.

GPC measurements were carried out against polystyrene standards in dimethylacetamide as solvent, using a RI detector. Concentration of the copolymer in the testing solution was 0.5% wt/vol.

[00116] **Step 2 – Stabilization, Hydrolysis and Dissolution in water**

[00117] 250 g of the powder obtained in Step 1 was treated at 70°C with a mixture of 10 L/h of fluorine and 4 L/h of nitrogen for 3 h end-capping the backbone with $–CF_3$ functional groups and removing the undesired carboxylic acid groups. The powder was treated under stirring with a 1.5 L

solution of $NaOH/H_2O$ (20 wt%) and heated at 80°C. Complete conversion of the originally comprised $–SO_2F$ groups to ionic $–SO_3^-$ groups was confirmed by solid state NMR. The amount of ionic groups in the polymer was 1.39 meq/g. After 10 h the powder was washed under stirring with deionized water (4x 1 L) for 30 min and dissolved in deionized water in a pressurized vessel heated at 250°C.

[00118] **Polymerization Example 2: Polymerization of tetrafluoroethylene (TFE) and perfluoro-5-sulfonylfluoride-3-oxa-1-pentene (SFVE) in the presence of dispersant (D-1)**

[00119] In a 5 L autoclave the following reagents were charged:

- 1.8 L of demineralized water;
- 20 g of a 25 wt% aqueous dispersion of dispersant (D-1) (i.e. corresponding to 5 g of dispersant (D-1)), obtained from Preparative Example 1, thus corresponding to a concentration of about 1.05 wt % based on the initial aqueous phase.

The autoclave, stirred at 650 rpm, was heated at 50°C. A water based solution with 16 g/L of sodium persulfate was added in a quantity of 90 mL. The pressure was maintained at a value of 7.6 bar (abs.) by feeding tetrafluoroethylene (TFE).

82 g of SFVE were fed in the reactor and the pressure of the autoclave was maintained at constant value of 7.8 bar by feeding TFE and feeding SFVE (23 g) each 5% of TFE conversion. After 230 minutes, when a quantity of 340 grams of TFE and 443 g of SFVE were fed, the TFE feeding was stopped. By keeping constant stirring of 650 rpm the autoclave was cooled to ambient temperature the latex was discharged after being kept under air bubbling for 48 hours to strip away residual monomers from the polymerization, and then stored in a plastic tank. No signals of latex coagulation/precipitation were observed.

The latex so produced was characterized by laser light scattering for determining average particle size, which was found to be of 107 nm. The polymer thus obtained had an equivalent weight (EW) of 758 g/mol and a composition, measured through FT-IR, of TFE: 82.7 mol% and SFVE: 17.3 mol%.

Claims

1. A method for making a fluoropolymer comprising a plurality of hydrolysable groups [polymer (P)], said method comprising emulsion polymerising in an aqueous medium:
   - tetrafluoroethylene, and
   - at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group,

   in the presence of at least one radical initiator and at least one polyfunctional dispersant [dispersant (D)], said dispersant (D):
   - having a weight average molecular weight (M_w), as measured by GPC, of at least 15000 and at most 800000;
   - comprising a backbone chain comprising recurring units deriving from one or more ethylenically unsaturated monomers; and
   - comprising a plurality of ionic groups selected from the group consisting of $-SO_3X_a$ and $-COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.
2. The method of claim 1, wherein dispersant (D) has a molecular weight and a molecular weight distribution such that it is substantially free from fractions having molecular weight of less than 3000 as measured by GPC.
3. The method of claim 1 or 2, wherein dispersant (D) has a weight average molecular weight (M_w), as measured by GPC, of from 150000 to 600000, preferably from 180000 to 500000.
4. The method of any one of the preceding claims, wherein the amount of ionic groups in dispersant (D) is at least 1.00 meq/g and/or of at most 2.50 meq/g, with respect to the weight of dispersant (D).
5. The method of any one of the preceding claims wherein the amount of dispersant (D) is from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.
6. The method of any one of the preceding claims, wherein dispersant (D) is a polymer comprising recurring units deriving from at least one ethylenically unsaturated fluorinated monomer containing at least one group $-SO_2X$, with X being $-OX_a$, wherein X_a is H, an ammonium group or a monovalent metal; and

recurring units deriving from at least one ethylenically unsaturated fluorinated monomer free from -SO_2X groups.

7. The method of claim 6, wherein the at least one ethylenically unsaturated fluorinated monomer free from -SO_2X groups is tetrafluoroethylene.
8. The method of any one of the preceding claims wherein polymer (P) comprises recurring units deriving from at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group selected from the group consisting of –SO_2X and –COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group.
9. The method of any one of the preceding claims wherein polymer (P) comprises recurring units deriving from at least one ethylenically unsaturated fluorinated monomer containing at least one -SO_2X group, with X being a halogen.
10. The method of any one of the preceding claims wherein polymer (P) and dispersant (D) comprise recurring units deriving from at least one ethylenically unsaturated fluorinated monomer containing at least one -SO_2X group which is selected from the group consisting of:
    - sulfonyl halide fluoroolefins of formula: $CF_2=CF(CF_2)_pSO_2X$; wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein p is an integer between 0 and 10, preferably between 1 and 6, more preferably p is equal to 1, 2 or 3;
    - sulfonyl halide fluorovinylethers of formula: $CF_2=CF\text{-}O\text{-}(CF_2)_mSO_2X$, wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein m is an integer between 1 and 10, preferably between 1 and 6, more preferably between 2 and 4, even more preferably m equals 2;
    - sulfonyl halide fluoroalkoxyvinylethers of formula: $CF_2=CF\text{-}(OCF_2CF(R_{F1}))_w\text{-}O\text{-}CF_2(CF(R_{F2}))_ySO_2X$
      wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein w is an integer between 0 and 2, R_{F1} and R_{F2}, equal or different from each other, are independently F, Cl or a C_1-C_{10} fluoroalkyl group, optionally substituted with one or more ether oxygens, y is

an integer between 0 and 6; preferably w is 1, R_{F1} is $-CF_3$, y is 1 and R_{F2} is F;

- sulfonyl halide aromatic fluoroolefins of formula $CF_2=CF-Ar-SO_2X$ wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein Ar is a C_5-C_{15} aromatic or heteroaromatic group.

11. The method of any one of the preceding claims wherein polymer (P) and dispersant (D) comprise:

- 50 to 99 mol%, with respect to total moles of polymer (P) or dispersant (D), of recurring units deriving from tetrafluoroethylene;

- 1 to 50 mol%, with respect to total moles of polymer (P) or dispersant (D), of recurring units deriving from at least one monomer selected from the group consisting of:

(j) sulfonyl halide fluorovinylethers of formula: $CF_2=CF-O-(CF_2)_mSO_2X$, wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein m is an integer between 1 and 10, preferably between 1 and 6, more preferably between 2 and 4, even more preferably m equals 2;

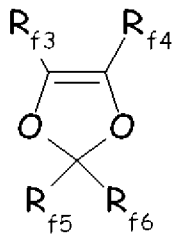
(jj) sulfonyl halide fluoroalkoxyvinylethers of formula: $CF_2=CF-(OCF_2CF(R_{F1}))_w-O-CF_2(CF(R_{F2}))_ySO_2X$

with X being OX_a, wherein in dispersant (D) X is OX_a, with X_a being H, an ammonium group or a monovalent metal and in polymer (P) X is a halogen, preferably F or Cl, more preferably F, wherein w is an integer between 0 and 2, R_{F1} and R_{F2}, equal or different from each other, are independently F, Cl or a C_1-C_{10} fluoroalkyl group, optionally substituted with one or more ether oxygen atoms, y is an integer between 0 and 6; preferably w is 1, R_{F1} is $-CF_3$, y is 1 and R_{F2} is F; and

(jjj) mixtures thereof; and

- 0 to 40 mol%, with respect to total moles of polymer (P) or dispersant (D), of recurring units deriving from at least one hydrogenated and/or fluorinated monomer different from tetrafluoroethylene, preferably a perfluorinated monomer selected from the group consisting of hexafluoropropylene, perfluoroalkylvinylethers of formula $CF_2=CFOR'_{f1}$, wherein R'_{f1} is a C_1-C_6 perfluoroalkyl; perfluoro-oxyalkylvinylethers of formula $CF_2=CFOR'_{O1}$, wherein

R'_{O1} is a C_2-C_{12} perfluoro-oxyalkyl having one or more ether groups, including perfluoroalkyl-methoxy-vinylethers of formula $CF_2=CFOCF_2OR'_{f2}$ in which R'_{f2} is a C_1-C_6 perfluoroalkyl, or a C_1-C_6 perfluorooxyalkyl having one or more ether groups; fluorodioxoles, of formula:



wherein each of R_{f3}, R_{f4}, R_{f5}, R_{f6}, equal or different each other, is independently a fluorine atom, a C_1-C_6 fluoro(halo)fluoroalkyl, optionally comprising one or more oxygen atom.

12. The method of any one of the preceding claims which comprises the step of preparing dispersant (D) by emulsion polymerising in an aqueous medium: tetrafluoroethylene, and at least one ethylenically unsaturated fluorinated monomer comprising at least one hydrolysable group selected from $-SO_2X$ and -COOZ, wherein X is a halogen atom and Z is a C1-C4 alkoxy group, in the presence of at least one radical initiator and a dispersant (Dx) to obtain a polymer comprising a plurality of hydrolysable groups; and hydrolysing the hydrolysable groups to obtain corresponding ionic groups $–SO_3X_a$ and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.
13. The method of claim 12 in which dispersant (Dx) is present in an amount from 0.01 wt% to 5.00 wt%, based on the total weight of the aqueous medium.
14. The method of claim 11 or 12 wherein dispersant (Dx) is dispersant (D).
15. An aqueous dispersion of particles of a fluoropolymer comprising a plurality of hydrolysable groups [polymer (P)], said dispersion comprising at least one dispersant (D), said dispersant (D):

    - comprising a backbone chain comprising recurring units deriving from one or more ethylenically unsaturated monomers,

    - having a weight average molecular weight (M_w) of at least 15000 and at most 800000,

    - comprising a plurality of ionic groups selected from the group consisting of –

SO_3X_a and $–COOX_a$, wherein X_a is H, an ammonium group or a monovalent metal.

16. A method for obtaining polymer (P) in its ionic form as a powdery material [material (PP)], said method comprising:
(1) : providing the aqueous dispersion of claim 15; and
(2): contacting said aqueous dispersion with a basic hydrolysing agent to at least partially convert the hydrolysable groups of polymer (P) into corresponding ionic groups, without causing any significant coagulation, so as to obtain an aqueous dispersion of particles of polymer (P) in ionic form; and optionally (3) : contacting the dispersion obtained at the end of step (2) with at least one ion exchange resin, so as to at least partially remove residues of basic hydrolysing agent and/or other contaminants; and
(4): spray drying the dispersion obtained at the end of step (2) and the optional step (3) so as to obtain the material (PP).
17. The method of claim 16 in which the hydrolysable groups are groups $-SO_2X$ and –COOZ , wherein X is a halogen atom and Z is a C1-C4 alkoxy group.
18. The method of claim 16 or 17 which comprises a further purification step which is performed between steps (2) and (4), in particular, when optional step (3) is present, between steps (3) and (4).
19. The method of claim 18 wherein the purification step is performed by means of one selected from dialysis, electrodialysis and ultrafiltration.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/054775

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F8/12 C08F8/22 C08F14/26 C08F214/26 C09D127/18
C08F259/08
ADD. C08F2/26
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)
C08F C08L C09D

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.
Y	WO 2006/119224 A1 (3M INNOVATIVE PROPERTIES CO [US]) 9 November 2006 (2006-11-09) example 1 page 8, lines 14-16	1-19
Y	WO 2018/167190 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 20 September 2018 (2018-09-20) cited in the application examples 1,2	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 May 2023	30/05/2023

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/054775

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006119224 A1	09-11-2006	CN 101171271 A	30-04-2008
		EP 1877454 A1	16-01-2008
		JP 5166248 B2	21-03-2013
		JP 5973319 B2	23-08-2016
		JP 2008540738 A	20-11-2008
		JP 2013232393 A	14-11-2013
		JP 2016104854 A	09-06-2016
		KR 20080003857 A	08-01-2008
		US 2006252888 A1	09-11-2006
		US 2007185220 A1	09-08-2007
		WO 2006119224 A1	09-11-2006
WO 2018167190 A1	20-09-2018	CN 110573541 A	13-12-2019
		CN 115433300 A	06-12-2022
		EP 3596144 A1	22-01-2020
		JP 2020510737 A	09-04-2020
		KR 20190126389 A	11-11-2019
		US 2020017621 A1	16-01-2020
		WO 2018167190 A1	20-09-2018