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(54) Title: PROCESS FOR THE MANUFACTURE OF FLUOROPOLYMER

(57) Abstract: The present invention relates to a process for the preparation of a fluoropolymer by polymerization of an aqueous dispersion of at least one fluoromonomer, this dispersion additionally comprising a fluorosurfactant, a radical initiator, optionally a transfer agent and optionally a paraffin wax, in which process the fluorosurfactant is chosen from one or more of the following products: $R_f(CH_2CF_2)_{m-1}$- $(CH_2)_nCO_2M$ [1] $R_f(CH_2CF_2)_mSO_2M$ [2] R_f $(CH_2$ $CF_2)_m(CH_2)_n'SO_3M$ [3] in which R_f is a linear or branched perfluoroalkyl group comprising from 1 to 5 carbon atoms, preferably from 2 to 4, m is an integer from 2 to 6, n is an integer from 0 to 2, n' is 0 or 2, M is a hydrogen atom or an alkali metal atom or an ammonium group or an ammonium group comprising at least one lower alkyl substituent. By way of example, the process of the invention is of use in the polymerization (homo- or copolymerization) of fluorovinyl monomers, such as, for example, tetrafluoroethylene C_2F_4 (TFE), vinylidene fluoride $H_2C=CF_2$ (VDF), hexafluoropropene $CF_2=CF-CF_3$ (HFP).

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Field of the invention

PROCESS FOR THE MANUFACTURE OF FLUOROPOLYMER

The present invention relates to a process for the preparation of a fluoropolymer by polymerization of an aqueous dispersion of fluoromonomers. These fluoromonomers can be chosen from vinylidene fluoride ($CF_2=CH_2$, also denoted by the abbreviation VDF), trifluoroethylene, chlorotrifluoroethylene, hexafluoropropene, vinyl fluoride or perfluoro(methyl vinyl ether).

Generally, as is taught in the state of the art, such aqueous dispersions of fluoromonomers comprise a fluorosurfactant, a radical initiator, optionally a chain-transfer agent and optionally a paraffin wax. The surfactants used to date could be biopersistent and bioaccumulable. The process of the present invention uses surfactants which do not exhibit these disadvantages.

The prior art and the technical problem

The polymerization of fluoromonomers requires the use of surfactants, themselves also fluorinated, which have noteworthy properties. The very strong C-F bonds and the characteristics of the fluorine atoms (high electronegativity, small size and low polarizability) confer excellent emulsifying properties, good thermal stability and good chemical stability. Although different kinds of them exist, the salts of carboxylic or sulphonic acids constitute the most frequently employed products. In particular, the perfluorocarboxylic acids under the generic names of PFOA (perfluorooctyl acid $C_7F_{15}COOH$ in the form of ammonium or lithium salts) or of APFO (ammonium perfluorooctanoate) are by far the most widely used industrially, all the more so since, because of the absence of terminations by hydrogen transfer, they are until now the only ones which allow PTFE elastomers of very high molar masses to be obtained. These surfactants could be biopersistent and bioaccumulable. It has been found that partially fluorinated surfactants would not exhibit these disadvantages.

Patents **US 5 998 521** and **US 6 013 795** disclose the synthesis and the use of α-branched surfactants for emulsion polymerization. The general formula of this class of surfactants is as follows:

$[Rf\text{-}CF(Rf')]_p\text{-}C(=O)X$, in which:

- Rf denotes a perfluoroalkyl chain (6 to 19 carbons),

- Rf' denotes a perfluoroalkyl chain (1 to 10 carbons),
- X=OM and M=NH_4, Li, Na, K or H.

These exhibit the advantage of not being bioaccumulable. These surfactants have a branching in the position α to the acid functional group which weakens the molecule and improves its biodegradability. In particular, these surfactants can be decomposed by heat treatment. One of these surfactants is $C_7F_{15}CF(CF_3)$-$COONH_4$. It is applicable to the polymerization of TFE or VDF and the copolymerization of HFP and VDF.

The prior art has already described the use of partially fluorinated surfactants to prepare fluoropolymers.

Patent **FR 2 286 153** (= US 4 025 709) discloses a process for the emulsion polymerization or copolymerization of VDF in the presence of surfactants of Rf-C_2H_4-SO_3M type where M is an ion with a valency of 1 and Rf is a perfluoroalkyl comprising from 4 to 10 carbon atoms. The process makes it possible to obtain polymers with a molecular mass which can be adjusted as desired.

Patent **WO 97/08214** discloses the use of sulphonic derivatives of the $C_6F_{13}C_2H_4SO_3M$ type, M being a cation with a valency of 1, for the polymerization in an aqueous medium of fluoromonomers. It applies to the polymerization of tetrafluoroethylene (TFE) and to its copolymerization with VDF or perfluoroolefins or perfluoro(vinyl ether)s. The advantage of this surfactant is toxicological. This is because it is much less bioaccumulable than PFOAs, whereas its C_8 homologue: $C_8F_{17}C_2H_4SO_3M$, is more bioaccumulable than the C_6 homologue. These surfactants, when they are present in the form of the ammonium salt, can result in thermal instability of the fluoropolymers.

Patent **US 5 763 552** discloses partially fluorinated compounds of formula:

$Rf(CH_2)_mRf'$-CO_2M, in which:

- Rf = C_{3-8} perfluoroalkyl or C_{3-8} perfluoroalkoxy,
- Rf' = C_{1-4} perfluoroalkylene,
- M = NH_4, Li, Na, K or H
- m = 1-3.

The distinguishing feature of these compounds is the presence of an alkylene group $(CH_2)_m$ positioned between two perfluorinated groups (R_f and R'_f). According to the inventors, the transfer of hydrogen with this type of surfactant is less significant than with a conventional surfactant, such as perfluoroethylsulphonates ($RfC_2H_4SO_3M$). These compounds prove to be of use in the emulsion polymerization of fluoromonomers (TFE, VDF or HFP). The polymers obtained (PTFE or others) exhibit a high molecular weight despite the presence of hydrogen in the surfactant. These surfactants exhibit bioaccumulation characteristics which are enhanced with the length of the perfluorinated chains but those having short perfluorinated chains are not very effective in the stabilization of PVDF latexes.

Patent Application **EP A1-0816397** discloses a process for the microemulsion polymerization of VDF in the optional presence of 0.1 to 10 mol% of one or more other fluorocomonomers. The microemulsion comprises a (per)fluoropolyether having neutral end groups or fluoropolyoxyalkylenes and a surfactant based on (per)fluoropolyethers having carboxylate end groups, preferably sodium carboxylate end groups. The fluoropolymers have an improved whiteness index and their level of residual surfactant is lowered and can reach 70 p.p.m. This type of perfluoropolyether-based surfactant, in particular those of low mass, are the most effective. However, they exhibit the disadvantage of being toxic.

Patent **FR 2 220 504** discloses the preparation of the acids $R_f(CH_2CF_2)_{m-1}CH_2$-COOH by reaction of nitric acid with $R_f(CH_2CF_2)_mI$ with $R_f = C_{3-14}$ and m = 1-3.

Patent **FR 2 220 505** discloses the acids $Rf[CH_2C(R1)F]_mCH_2CH_2$-COOH in which $Rf = C_{4-12}$ perfluoroalkyl, R1 = H or F and m = 1-3. Obtained by hydrolysis of the corresponding nitriles, they are used in the preparation of products for the hydrophobic and oleophobic treatment of porous substrates. Nothing suggests their use as surfactant in the preparation of fluoropolymers.

It has now been found that surfactants comprising at least two $-(CH_2-CF_2)-$ units are suitable for the manufacture of fluoropolymers without exhibiting the abovementioned disadvantages.

Brief description of the invention

The present invention relates to a process for the preparation of a fluoropolymer by polymerization of an aqueous dispersion of at least one fluoromonomer, this dispersion additionally comprising a fluorosurfactant, a radical initiator, optionally a transfer agent and optionally a paraffin wax, in which process the fluorosurfactant is chosen from one or more of the following products:

$$R_f(CH_2CF_2)_{m-1}\text{-}(CH_2)_nCO_2M \quad [1]$$

$$R_f(CH_2CF_2)_mSO_2M \quad [2]$$

$$R_f(CH_2CF_2)_m(CH_2)_{n'}SO_3M \quad [3]$$

in which:

- R_f is a linear or branched perfluoroalkyl group comprising from 1 to 5 carbon atoms, preferably from 2 to 4,
- m is an integer from 2 to 6,
- n is an integer from 0 to 2,
- n' is 0 or 2,
- M is a hydrogen atom or an alkali metal atom or an ammonium group or an ammonium group comprising at least one lower alkyl substituent. The term "lower alkyl" is understood to mean a number of carbon atoms of at most 4 and generally having the value 2 or 3.

Ammonium salts are advantageously used. They have the advantage of resulting in polymers of high purity. In the general case, the choice will be made of a counterion which prevents yellowing of the polymer during heat treatments. Advantageously, in the formulae [1] to [3], m = 3, 4 or 5.

The process of the invention exhibits the following advantages:

- lower biopersistence related to a number of CF_2 units in the surfactant of at most 5 and advantageously of 4,
- reduced ability to become concentrated in the cells; this ability can be modelled by calculation of log of Kow as defined later in the text,

- good thermal stability, in particular of PVDF comprising surfactant residues in the ammonium form which can range up to 1000 ppm. This result is unexpected, in view of the very poor thermal stability of PVDFs comprising between 300 and 1000 ppm of $C_7F_{15}COONH_4$ or $C_8F_{17}COONH_4$.

By way of example, the process of the invention is of use in the polymerization (homo- or copolymerization) of fluorovinyl monomers, such as, for example, tetrafluoroethylene C_2F_4 (TFE), vinylidene fluoride $H_2C=CF_2$ (VDF), hexafluoropropene $CF_2=CF-CF_3$ (HFP).

The polymerizations of the process of the invention are generally initiated by radical initiators from the family of organic peroxides, peresters, such as percarbonates or perpivalates, or inorganic persalts, such as potassium persulphate or ammonium persulphate. Preferably, the radical initiator employed represents from 0.05 to 1% by weight with respect to the total weight of the fluoromonomer(s) employed. The polymerization is generally carried out at pressures of 40 to 120 bar and between 40 and 130°C, preferably between 50 and 90°C. The amount of surfactant necessary depends on the concentration of monomer in the dispersion. It also depends on the size of the polymer particles required. Advantageously, the fluorosurfactant employed represents from 0.05 to 0.5% by weight with respect to the total weight of the fluoromonomer(s) employed.

The polymerization in aqueous dispersion can be carried out in the presence of a paraffin wax with a melting point ranging from 40 to 70°C and representing from 0.005 to 0.1% by weight with respect to the total weight of the fluoromonomer(s). The molar masses can be adjusted by addition of a chain-transfer agent.

The polymer can be isolated by conventional methods, such as precipitation, by addition of an electrolyte or of a solvent, by conversion to a dry powder by spray-drying or by freeze drying. The latex can also be stabilized for applications by coating or impregnation.

Depending on the nature of the surfactant and its proportions, the process is said to be an “emulsion” process or any other process derived from

the emulsion (microsuspension, miniemulsion, and the like) which are fully known to a person skilled in the art. After the end of the polymerization, the fluoropolymer is separated from the water and from the possible residues of the reactants used.

In the case of the emulsion-type processes, the polymer is present in the form of a latex composed of very fine particles, the mean diameter of which is generally less than 1 micron. This latex can be coagulated and optionally concentrated by removing a portion of the water, for example by centrifuging. In the coagulated state, it is also possible to obtain an aerated cream, less dense than water, which can be washed with deionized water according to techniques already described in the prior art (Patents US 4 218 517 and EP 0 460 284). The washed cream can then be dried by bringing it into contact with a hot gas in an spray-dryer and the fluoropolymer is collected as a powder. This technique is known and used in processes for the manufacture of PVDF.

The effectiveness of the surfactant in the polymerization can be characterized by the yield, the level of flocculate, its residual level after spray-drying and the thermal stability of the polymer in the dry powder form.

The invention is of particular use for the preparation of PVDF homopolymer or copolymer.

The products of formula [1] in which R_f is C_2F_5 and m = 4 or 5 and the products of formulae [2] and [3] are novel as products. The invention relates to these products.

Detailed description of the invention

As regards the fluoropolymer, this term is used to denote any polymer having, in its chain, at least one monomer chosen from compounds comprising a vinyl group capable of opening in order to polymerize and which comprises, directly attached to this vinyl group, at least one fluorine atom, one fluoroalkyl group or one fluoroalkoxy group.

Mention may be made, as examples of monomer, of vinyl fluoride; vinylidene fluoride (VDF); trifluoroethylene (VF3); chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene

(HFP); or perfluoro(alkyl vinyl) ethers, such as perfluoro(methyl vinyl) ether (PMVE), perfluoro(ethyl vinyl) ether (PEVE) and perfluoro(propyl vinyl) ether (PPVE).

The fluoropolymer can be a homopolymer or a copolymer; it can also comprise nonfluorinated monomers, such as ethylene.

By way of examples, the fluoropolymer is chosen from:

- homo- and copolymers of vinylidene fluoride (VDF) preferably comprising at least 50% by weight of VDF, the comonomer being chosen from chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE),
- homo- and copolymers of trifluoroethylene (VF3),
- copolymers, and in particular terpolymers, combining the residues of the chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and/or ethylene units and optionally of the VDF and/or VF3 units.
- homo- and copolymers of tetrafluoroethylene (TFE) preferably comprising at least 50 % by weight of TFE.

Advantageously, the fluoropolymer is poly(vinylidene fluoride) (PVDF) homopolymer or copolymer. Preferably, the PVDF comprises, by weight, at least 50% of VDF, more preferably at least 75% and better still at least 85%. The comonomer is advantageously HFP.

As regards the radical initiator, this term is used to denote any generator of radicals which is capable of bringing about the polymerization of the fluoromonomers in the process described above. Preferably, the radical initiator employed represents from 0.05 to 1% by weight with respect to the total weight of the fluoromonomer(s) employed.

The initiator can be organosoluble. Mention may be made essentially of hydrocarbonaceous peroxides, such as di(tert-butyl) peroxide, dicumyl peroxide or benzoyl peroxide, dialkyl peroxydicarbonates, such as diethyl or diisopropyl peroxydicarbonate or di(n-propyl) peroxydicarbonate, peracids or peresters, such as t-butyl perpivalate, t-amyl perpivalate or t-butyl peroxybenzoate.

The initiator can be a persulphate, advantageously an alkali metal persulphate and preferably a potassium persulphate or an ammonium persulphate.

As regards the transfer agent, this term is used to denote any product which makes it possible to limit the molar mass of the polymer while propagating the polymerization reaction. It generally exhibits a hydrogen bond sensitive to a radical attack. Mention may be made, by way of example, of ethane, propane, acetone, isopropanol, methyl acetate, ethyl acetate, diethyl ether, methyl tert-butyl ether, n-butyl acetate, diethyl malonate, diethyl carbonate, HFA161 (CH_3-CH_2F) and various chlorofluorocarbon compounds. The amount of transfer agent depends essentially on its nature and on the average molar mass desired for the polymer fraction obtained in its presence, which conditions the mean viscosity of the final product. Preferably, the transfer agent employed represents from 0.05 to 5% by weight with respect to the PVDF manufactured. Advantageously, ethyl acetate is used.

Advantageously, in addition to the surfactant, a paraffin wax is also added. The paraffin wax employed has a melting point ranging from 40 to 70°C and represents from 0.005 to 0.1% by weight with respect to the total weight of the fluoromonomers.

As regards the implementation of the process, according to an advantageous form, the invention is a batchwise or semicontinuous process for the manufacture of fluoropolymer, in which:

- water, the surfactant and optionally a paraffin wax are charged to the polymerization reactor,
- the reactor is deaerated to remove the oxygen,
- the reactor is brought to the chosen temperature and the fluoromonomer and optionally one (or more) optional comonomer(s) are charged until the desired pressure is reached,

- the optional transfer agent is introduced into the reactor, either in its entirety or partly at the start and partly during the polymerization,
- the initiator is added, in all or in part, to initiate the polymerization, and the fall in pressure which results therefrom is compensated for by the addition of fluoromonomer and optional comonomer,
- the possible remainder of the initiator is added during the polymerization,
- after introduction of the planned amount of fluoromonomer and optional comonomer, the reactor is degassed and the fluoropolymer is separated by any means from the water and possible residues of the reactants used.

The temperature chosen is the temperature which is sufficient to polymerize the monomers and is of the order of 45 to 130°C. The desired pressure is of the order of 40 to 120 bar.

The volume of water in which the monomers are dispersed and the amounts of surfactant, initiator and transfer agent can be easily determined by a person skilled in the art. The polymerization is carried out in a stirred reactor and then the fluoropolymer (it is in the form of solid particles) and the water are separated by any means. These techniques are known per se and are described in Patents US 4 025 709, US 4 569 978, US 4 360 652, EP 626 396 and EP 0 655 468.

Another possible embodiment is now described. After charging the polymerization reactor with water, surfactant, optionally paraffin wax, transfer agent, in all or in part, and radical initiator, in all or in part, the reactor is pressurized, after having removed the oxygen, by adding thereto a fluoromonomer, alone or as a mixture with another unsaturated fluoromonomer, and the mixture is brought to the chosen temperature.

During the polymerization, the fluoromonomer(s) is/are added to maintain the pressure, along with initiator, incrementally or by continuous addition. The transfer agent can be added at the start or during the polymerization.

After introduction of the planned amount of fluoromonomer(s), the reactor is degassed and the fluoropolymer dispersion emptied. This dispersion is denoted by latex in emulsion processes.

The latex is diluted and then introduced into a coagulator, where it is subjected to shearing in the presence of air. Under the combined effect of these two actions, the latex is converted into an aerated slurry where the density is lower than that of water.

This slurry can be washed countercurrentwise with deionized water according to the process disclosed in EP 0 460 284. The washing stage makes it possible to remove water-soluble entities incorporated before the polymerization or generated during the polymerization. At the outlet of the washing column, the aerated slurry is conveyed to a storage container before being directed, by pumping, to an spray-dryer, where it is converted to a dry powder. It is also possible to atomize the slurry without preliminary washing. This stage of drying in an spray-dryer can also be applied to the initial latex, optionally diluted, to the coagulated latex, for example coagulated by mechanical shearing, with or without preliminary dilution, or alternatively to the aerated cream.

Another possible embodiment is now described. An aqueous dispersion of the organosoluble radical initiator, stabilized by a surfactant which can be that used to carry out the polymerization, is prepared. To produce this dispersion, the water, the radical initiator and the surfactant are mixed in a disperser. It is this dispersion which is added at the beginning of and then optionally during the polymerization.

After charging the polymerization reactor with water, surfactant and optionally paraffin wax, the optional transfer agent is added, the reactor is pressurized, after having removed the oxygen, by adding thereto the fluoromonomer, alone or as a mixture with the comonomer, and the mixture is brought to the chosen temperature. Advantageously, the aqueous emulsion is polymerized at a temperature of 45 to 130°C. Preferably, the polymerization is carried out at an absolute pressure of 40 to 120 bar. The reaction is initiated by addition of the radical initiator dispersion.

During the polymerization, the fluoromonomer, alone or as a mixture with a comonomer, is optionally added to maintain the pressure or to obtain a controlled pressure variation. The radical initiator is optionally added, incrementally or continuously. After introduction of the planned amount of fluoromonomer(s), the reactor is degassed and the fluoropolymer dispersion emptied. The fluoropolymer can be recovered as described in the preceding process.

As regards the surfactant, M is advantageously ammonium. Advantageously, R_f comprises from 2 to 4 carbon atoms. Advantageously, m has the value of 3, 4 or 5. Advantageously, n has the value of 0 or 1. Use may be made of a mixture of surfactants, for example a mixture of products of formula [1] or of a product of any one of the formulae with at least one other product of another formula or of the other two formulae or any combination of these possibilities.

The surfactant is preferably chosen from one or more of the following products:

$C_2F_5(CH_2CF_2)_3$-$CH_2CO_2NH_4$

$C_2F_5(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_2F_5(CH_2CF_2)_3$-CO_2NH_4

$C_2F_5(CH_2CF_2)_2$-CO_2NH_4

$C_3F_7(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_3F_7(CH_2CF_2)_3$-CO_2NH_4

$C_4F_9(CH_2CF_2)_3$-CO_2NH_4

$C_4F_9(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_4F_9(CH_2CF_2)_2$-CO_2NH_4

$C_2F_5(CH_2CF_2)_3CH_2CH_2SO_3K$

$C_3F_7(CH_2CF_2)_2CH_2CH_2SO_3K$

$C_4F_9(CH_2CF_2)_3CH_2CH_2SO_3K$

$C_4F_9(CH_2CF_2)_2CH_2CH_2SO_3K$

The surfactant represents from 0.05 to 0.5% by weight, preferably 0.01 to 0.025%, with respect to the total weight of the fluoromonomers.

The advantage of such compounds is that of not comprising a perfluorinated chain of more than four carbon atoms, thus they are less capable of bioaccumulating. This nature depends on the relative ability of the surfactant to migrate into living cells. One method for simulating this property is accessible by calculation of the log Kow. The higher this value, the greater the risk of the substance migrating into the cells; thus, calculations have been carried out to compare a surfactant according to the invention with the most widely used products:

The calculation of Kow is given in detail in KOWWIN on the EPA site after encoding the molecular structures by the SMILES system (Weiniger D.J., Chem. Inf. Comput. Sci., 28 (1), 31-36) :

$C_2F_5(CH_2CF_2)_2$-CO_2NH_4	log Kow = 2.78
$C_2F_5(CH_2CF_2)_3$-CO_2NH_4	log Kow = 3.01
$C_8F_{17}CO_2NH_4$	log Kow = 6.65

In this process, the thermal stability of the fluoropolymer remains good despite a residual level of surfactant which can range up to 1000 ppm, unlike the surfactants of the $C_7F_{15}COONH_4$ and $C_8F_{17}COONH_4$ type of the prior art. This novel characteristic makes possible simplified finishing, such as drying by spray-drying or on a rotary drier without a preliminary washing stage. It is also possible, in the case of an emulsion process, to use a method for finishing the latex by coagulation and washing, as described in Patent US 4 128 517, which makes it possible to prepare a fluoropolymer possessing good thermal stability.

As regards the synthesis of PVDF,

the initiator is advantageously potassium persulphate, n-propyl peroxydicarbonate, isopropyl peroxydicarbonate, di(tert-butyl) peroxide, tert-butyl peroxypivalate or tert-amyl peroxypivalate.

The transfer agent is advantageously ethyl acetate, ethane, propane, diethyl malonate or diethyl carbonate.

The surfactant is advantageously:

C_2F_5-$(CH_2CF_2)_3$-$COONH_4$

C_2F_5-$(CH_2CF_2)_3$-CH_2-$COONH_4$

C_2F_5-$(CH_2CF_2)_2$-$COONH_4$

C_2F_5-$(CH_2CF_2)_2$-CH_2COONH_4

C_3F_7-$(CH_2CF_2)_3$-CH_2-$COONH_4$

C_4F_9-$(CH_2CF_2)_3$-CH_2-$COONH_4$

$C_2F_5(CH_2CF_2)_3CH_2CH_2SO_3K$

$C_4F_9(CH_2CF_2)_3CH_2CH_2SO_3K$

As regards the preparation of the surfactant of formula [1], the products with the structure $R_f(CH_2CF_2)_{m-1}$-$(CH_2)_nCO_2M$ can be obtained according to known techniques:

- by reaction of nitric acid with $R_f(CH_2CF_2)_m$-I and hydrolysis of nitrates,
- by reaction of oleum with $R_f(CH_2CF_2)_m$-I and hydrolysis of the sulphates,
- by reaction of oleum with the corresponding ethylenated derivatives $R_f(CH_2CF_2)_m$ CH_2 CH_2-I,
- by hydrolysis of the corresponding nitriles $R_f(CH_2CF_2)_mCH_2CH_2$-CN,
- by oxidation of corresponding olefins $R_f(CH_2CF_2)_mCH=CH_2$,
- by oxidation of the corresponding alcohols $R_f(CH_2CF_2)_{m-1}$-$(CH_2)_{n+1}OH$,
- by oxidation of the olefins $R_f(CH_2CF_2)_{m-1}$-$CH=CF_2$.

The iodinated precursors $R_f(CH_2CF_2)_m$-I are obtained, in a well known way, by telomerization of perfluoroalkyl iodide $C_nF_{2n+1}I$ with vinylidene fluoride, for example in the liquid phase in the presence of a radical initiator of peroxide type. The mixture resulting from the telomerization can be fractionated to isolate the various compounds with m = 1, 2, 3, 4, 5 or 6.

The olefins $R_f(CH_2CF_2)_{m-1}$-$CH=CF_2$ can be prepared, for example, by heating $R_f(CH_2CF_2)_m$-I in the presence of water and of triethylamine.

The olefins $R_f(CH_2CF_2)_{m-1}$-$CH=CF_2$ can be oxidized using conventional reagents, such as potassium permanganate or dichromate. However, it does not result in a single carboxylic acid as the attack of the oxidizing agent takes place both on the fluorinated carbon α to the olefin and, to a lesser extent, on the protonated carbon in the β position.

Another method for the synthesis of the carboxylic acids of formula [1] consists in starting from the corresponding sulphinates $R_f(CH_2CF_2)_m$-SO_2Na of

formula [2]. The sulphinates can be prepared by analogy with known techniques described in the perfluorinated series, for example by Chang-Ming Hu in J. Org. Chem., Vol. 56, No. 8, 1991, page 2803, by reaction of sodium hydrosulphite, (dithionite) with the iodinated derivative in a water/acetonitrile or water/ethanol medium in the presence of an alkaline earth metal neutralizing agent, preferably sodium hydrogenocarbonate. The conversion of the sulphinates can be carried out by analogy with the method described by Chinese researchers of the Shanghai Institute of Organic Chemistry, who, starting from perhalofluoroalkylated sulphinates and from an oxidizing or redox system $(NH_4)_2S_2O_8$, $Ce(SO_4)_2$ or H_2O_2/Fe^{2+}, have obtained perhalofluorocarboxylic acids (*Journal of Fluorine Chemistry*, 49, 1990, pp 433-437) and, by photooxidation under UV irradiation in methanol with a high-pressure mercury lamp at ambient temperature and in the presence of oxygen, have identified the corresponding methyl esters (*Tetrahedron Letters*, 30, No. 48, pp 6717-6720).

It has now been shown that it is possible to obtain the carboxylic acids $R_f(CH_2CF_2)_{m-1}$-CH_2COOH by dissolution of the sulphinates $R_f(CH_2CF_2)_m$-SO_2Na in water and generation of radicals using water-soluble radical initiators, such as certain azo compounds.

The amount of radical initiator can vary, for example, from 0.01 to 0.2 by molar ratio with respect to the sulphinate. It will preferably be added in solution and slowly, so as to generate the radicals little by little in order to avoid radical secondary reactions.

The reaction will preferably be carried out in a homogeneous medium in an organic solvent or in water at a concentration which can vary, depending on the solubility of the precursor sulphinates, from a few per cent to 70-80% by weight, preferably between 10 and 30%. The reaction temperature will depend on the radical initiator used. By way of example, it is between 45 and 70°C.

The reaction medium can be one or more polar organic solvents in which the sulphinates are soluble, such as, for example, alcohols, esters and ketones. In order to avoid secondary reactions, the choice will preferably be made of the ester which was used beforehand to extract the intermediate sulphinate from the aqueous solution, such as ethyl or isopropyl acetate.

In this case, use may be made of a radical initiator from the family of the commonest azo compounds, such as 2,2'-azobisisobutyronitrile (AZDN® from Atofina) or 2,2'-azobis(2-methylbutanenitrile) (Vazo®67 from DuPont).

It can be advantageous to carry out the reaction in an aqueous medium. As the majority of fluorosulphinates are soluble in water, a water-soluble azo radical initiator will be chosen, such as the following commercial products: 4,4'-azobis(4-cyanopentanoic acid) (Azocarboxy® from Atofina), 2,2'-azobis(2-amidinopropane) hydrochloride (V50 from Wako) or 2,2'-azobis[2-(2-imidazolin-2-yl)propane] hydrochloride (Vazo® 44WSP from DuPont).

The conversion of the sulphinates to carboxylic acids can advantageously be carried out in the reaction medium for the synthesis of the sulphinate precursors without isolation of the latter and without removing the by-products and inorganic salts before addition of the radical initiator.

The carboxylic acids formed can be isolated either by separation by settling or filtration or by extraction with an organic solvent and then evaporation of the latter.

As regards the preparation of the surfactant of formula [2], by reaction of sodium hydrosulphite (dithionite) with the iodinated derivative in a water/acetonitrile or water/ethanol medium in the presence of an alkaline earth metal neutralizing agent, preferably sodium hydrogenocarbonate.

As regards the preparation of the surfactant of formula [3],

the products of structure [3] $R_f(CH_2CF_2)_m$-$(CH_2)_{n'}SO_3M$

- with n' = 0, can be obtained by known techniques, such as:
  - oxidation of the sulphinates [2], for example by treatment with aqueous hydrogen peroxide solution,
  - oxidation of the sulphinates in the polymerization medium, as disclosed in Patents US 5 285 002 and US 5 639 837,
- with n' = 2, can be obtained by known techniques, such as:
  - methanolysis of the corresponding $R_f(CH_2CF_2)_mCH_2CH_2$-SO_2Cl compounds.

As regards the evaluation of the fluoropolymers and first of the thermal stability:

a sheet with dimensions of 260 × 20 × 4 mm is formed by compressive moulding, under 30 bar and at 205°C for 6 minutes, from 40 g of powder, which sheet is subjected to steeping in water at 20°C. The sheet is subsequently reheated in a Metrastat® PSD 260 oven at 265°C for 1 hour in the presence of air. After this heat treatment, the sheet can be more or less coloured. The colour is determined by a measurement of yellowing index. The sheet is placed on a calibrated white ceramic plate and the yellowing index is measured by a Minolta® CR 210 colorimeter using the ASTM D 1925 standard for the calculation of the yellowing index. To reduce the standard deviation of this measurement, the latter is repeated a further time and the value shown is a mean yellowing index with a standard deviation of 1.5.

Determination of the melt flow index:

This melt flow index is determined using a melt flow tester according to the ISO 1133 standard at a temperature of 230°C and a weight of 5 kg. The index is expressed according to the standard in g/10 min.

Examples

Example 1: Preparation of a mixture of $C_2F_5(CH_2CF_2)_3$-CO_2NH_4 and $C_2F_5(CH_2CF_2)_2$-$CH_2CO_2NH_4$ in the molar proportions 70/30.

a) Preparation of the telomer $C_2F_5(CH_2CF_2)_m$-I

1000 g of C_2F_5I and 7 g of catalyst (cyclohexyl percarbonate) are injected into a 3 l autoclave rendered inert beforehand with nitrogen. 413 g of vinylidene fluoride are then introduced with stirring. The mixture is maintained at 60°C under 25 bar for 6 hours. The telomer obtained is fractionated by distillation under reduced pressure to produce the various chain lengths m.

b) Preparation of the olefin $C_2F_5(CH_2CF_2)_{m-1}$-$CH=CF_2$

100 g of iodinated telomer $C_2F_5(CH_2CF_2)_4$-I and 33 g of water are introduced into a jacketed reactor heated using a thermostatically-controlled bath which is

equipped with a mechanical stirrer, an upright reflux condenser, a dropping funnel and a temperature probe. The mixture is heated beforehand to 40°C and 23.2 g of triethylamine are run thereon without exceeding 45°C; after 4 hours at 40°C, the reaction mixture is separated by settling, washed with water and then distilled at 68°C under 4 mbar. The olefin $C_2F_5(CH_2CF_2)_3$-CH=CF_2 is obtained with a yield of 80% and a purity of 99%.

c) Oxidation of the olefin to carboxylic acid:

18.7 g of the olefin, 110 g of water and 14.6 g of 96% H_2SO_4 are charged to a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, an upright reflux condenser, a dropping funnel and a temperature probe. The mixture is heated to 60°C and 24.9 g of $KMnO_4$ are added thereto little by little over 6 hours. The mixture is cooled and treated with Na_2SO_3, added slowly, to reduce the MnO_2, and the carboxylic acid is extracted with diisopropyl ether. After washing the organic phase with 100 ml of 5% H_2SO_4 and then drying over Na_2SO_4, the solvent is removed on a Rotavap® (rotary evaporator). The white solid, obtained with a yield of 97%, is analysed by NMR; it is a 70/30 molar mixture of

$C_2F_5(CH_2CF_2)_3$-CO_2H

$C_2F_5(CH_2CF_2)_2$-CH_2CO_2H

d) Preparation of the ammonium salt of the preceding mixture:

After quantitatively determining the carboxyl functional groups in an aqueous/alcoholic medium, a 15% aqueous solution is prepared by addition of aqueous ammonia to a pH of 6.9.

Example 2: Preparation of a 15% aqueous solution of $C_2F_5(CH_2CF_2)_3CH_2CO_2NH_4$

a) Synthesis of sodium polyfluoroalkylsulphinate: C_2F_5-$(CH_2$-$CF_2)_4$-SO_2Na

The following are introduced with stirring into a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer, an upright reflux condenser, a dropping funnel and a temperature probe: 180 g of demineralized water, 12.6 g of $NaHCO_3$ (0.15 mol) and 26.1 g of sodium hydrosulphite $Na_2S_2O_4$

(0.15 mol). A solution of 50.2 g of iodinated telomer C_2F_5-(CH_2-CF_2)$_4$-I (0.1 mol) in 48 g of ethanol is added dropwise using the dropping funnel and then the reaction medium is heated at reflux for 4 hours. After removing the ethanol by distillation, the sulphinate obtained is extracted with ethyl acetate and the organic phase is washed with a saturated NaCl solution and dried over Na_2SO_4. The solvent is subsequently removed by distillation on a rotary evaporator under reduced pressure at T < 60°C. The sulphinate is obtained in the form of a white solid with a melting point of 86°C, with a yield of 95%.

b) The sulphinate can be converted to carboxylic acid by four different processes, b1 to b4.

b1) Treatment of the sulphinate with water:

45.9 g of sulphinate are dissolved in 600 g of demineralized water and are kept stirred for several hours. The pH changes from 6 to 1. The white precipitate formed is filtered off on a sintered glass funnel and then a further precipitate is formed in the filtrate. After a few weeks, the precipitates, which are of the same nature (characteristic band in the IR spectrum of the –COOH groups at 1706 cm^{-1}), are combined. The NMR analysis shows that it is essentially carboxylic acid $C_2F_5(CH_2CF_2)_3$-CH_2CO_2H with an overall yield of approximately 90% and a melting point of 78°C.

b2) Treatment of the sulphinate with ammonium persulphate:

4.62 g of sulphinate [3] (0.01 mol), 60 g of demineralized water and 2.28 g of $(NH_4)_2S_2O_8$ are charged to a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, an upright reflux condenser and a temperature probe. The mixture is heated at 63°C for 5 hours. The gel formed is extracted with 60 g of diisopropyl ether. The organic phase is washed with water and then dried over Na_2SO_4. After evaporating the solvent under vacuum, a white solid with a melting point of 74°C is collected with a yield of 78%. It exhibits the same spectral characteristics as the carboxylic acid $C_2F_5(CH_2CF_2)_3$-CH_2CO_2H.

b3) Treatment of the sulphinate with a redox couple $FeSO_4/H_2O_2$:

4.62 g of sulphinate (0.01 mol), 35 g of demineralized water and 0.93 g of iron sulphate heptahydrate are charged to a 250 ml three-necked round-bottomed

flask equipped with a mechanical stirrer, an upright reflux condenser and a temperature probe. The mixture obtained is cooled to 0°C using an ice bath and a solution of 8.57 g of 35% aqueous hydrogen peroxide solution diluted by 15 g of water is run in dropwise. After 18 hours at ambient temperature, the mixture is acidified with 96% H_2SO_4. The gel obtained is then extracted with 55 g of diisopropyl ether. The organic phase is washed with water and then dried over Na_2SO_4. After evaporating the solvent under vacuum, a white solid with a melting point of 74°C is collected with a yield of 81%. It exhibits the same spectral characteristics as the carboxylic acid $C_2F_5(CH_2CF_2)_3$-CH_2CO_2H.

b4) Treatment of the sulphinate with an azo radical initiator

4.62 g of sulphinate (0.01 mol) and 30 g of demineralized water are charged to a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, an upright reflux condenser and a temperature probe. The mixture is heated to 55°C and then a solution of 0.34 g of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (Aldrich) in 20 g of water is added thereto dropwise over 1h 30. After stirring at 55°C for 5 hours, the gel formed is separated by settling and then extracted with diisopropyl ether. The organic phase is washed with water to a pH of 3.5 and then dried over Na_2SO_4. After evaporating the solvent under vacuum, a white solid with a melting point of 77°C is collected with a yield of 88%. It exhibits the same spectral characteristics as the carboxylic acid $C_2F_5(CH_2CF_2)_3$-CH_2CO_2H.

c) Preparation of an aqueous solution of $C_2F_5(CH_2CF_2)_3CH_2CO_2NH_4$

After quantitatively determining the carboxyl functional groups in an aqueous/alcoholic medium, a 15% aqueous solution of $C_2F_5(CH_2CF_2)_3CH_2CO_2NH_4$ is prepared by addition of aqueous ammonia to a pH of 6.9.

Example 3: Polymerization of VDF.

The following are successively introduced at 20°C into a 28 l horizontal reactor made of stainless steel:

17.9 l of deionized water,

200 g of a 15% aqueous solution, prepared in Example 1d, of a 70/30 molar mixture of $C_2F_5(CH_2CF_2)_3CO_2NH_4$ and $C_2F_5(CH_2CF_2)_2CH_2CO_2NH_4$,

1.4 g of paraffin wax with a melting point of approximately 60°C,

2.5 g of sodium acetate trihydrate.

The reactor is closed, the air is driven off using a vacuum pump and the medium is placed under stirring and brought to 83°C. Vinylidene fluoride is then introduced up to an absolute pressure of 45 bar and then 88 g of ethyl acetate and 150 g of a 1% (by weight) potassium persulphate solution are added. The polymerization begins and the medium is maintained at 83°C and the VDF pressure is maintained at 45 bar by continuous addition of monomer.

After polymerizing for 1h 30 and 2h 30, 50 g of the 1% $K_2S_2O_8$ solution are again added. After having introduced a total of 8.5 kg of VDF, this introduction is halted and the gas pressure in the reactor falls to 15 bar. The unreacted VDF monomer is degassed. 27.2 kg of latex, having a solids content of 30.2% by weight of solid matter, are obtained. The amount of coagulate formed during the polymerization is less than 1% as dry weight of PVDF formed. The latex is diluted, so as to bring its solids content to 20%, and is then spray-dried in a 1 m^3 spray-dryer. The temperature of the air introduced into the spray-dryer is 140°C; the water is removed at a flow rate of 7 kg/h. A portion of the surfactant is removed during the drying. The ^{19}F NMR analysis gives a residual level of surfactant of 900 ppm. Despite this high level, the thermal stability, evaluated after heating at 265°C for 1 hour, is good (yellowing index = 32). The melt flow index is 3.5 g/10 min.

Example 4: Polymerization of VDF

The following are successively introduced at 20°C into a stirred reactor described in Example 3:

17.9 l of deionized water,

141 g of a 15% aqueous solution of a surfactant of formula $C_2F_5(CH_2CF_2)_3CH_2CO_2NH_4$ prepared in Example 2,

1.4 g of paraffin wax with a melting point of approximately 60°C.

The reactor is closed, the air is driven off using a vacuum pump and the medium is placed under stirring and brought to 83°C. Vinylidene fluoride is then introduced up to an absolute pressure of 45 bar and then 54 ml of ethyl acetate and 20 g of a 30% by weight solution of n-propyl peroxydicarbonate in methyl pivalate are added. The polymerization begins and the medium is maintained at 83°C and the VDF pressure is maintained at 45 bar by a continuous addition of monomer, while the solution of n-propyl peroxydicarbonate in methyl pivalate is introduced at a constant flow rate of 13 g/hour. After having introduced a total of 7 kg of VDF monomer, the introductions of monomer and of initiator are halted and the gas pressure in the reactor falls to 15 bar. The unreacted VDF monomer is degassed. 24.4 kg of latex having a solids content of 26% are obtained. The amount of coagulate formed during the polymerization is 1.5% as dry weight of PVDF formed. The latex is diluted, so as to bring its solids content to 20%, and is then spray-dried in a 1 m^3 spray-dryer. The temperature of the air introduced into the spray-dryer is 140°C; the water is removed at a flow rate of 7 kg/h. The ^{19}F NMR analysis gives a residual level of surfactant of 700 ppm. The thermal stability, evaluated after heating at 265°C for 1 hour, is good (yellowing index = 31). The melt flow index is 1.3 g/10 min.

Comparative example

The surfactant used in Example 4 is replaced by 141 g of a 15% solution of a mixture of ammonium perfluoroalkylate corresponding to the overall formula $C_{8.4}F_{17.8}COONH_4$. The polymerization and the treatment for recovery of the polymer take place as in Example 4. After a heat treatment at 265°C for 1 hour, the PVDF formed in the comparative example is more coloured than the PVDF produced in Example 4. The yellowing index is 45.

CLAIMS

1 Process for the preparation of a fluoropolymer by polymerization of an aqueous dispersion of at least one fluoromonomer, this dispersion additionally comprising a fluorosurfactant, a radical initiator, optionally a transfer agent and optionally a paraffin wax, in which process the fluorosurfactant is chosen from one or more of the following products:

$$R_f(CH_2CF_2)_{m-1}-(CH_2)_nCO_2M \quad [1]$$

$$R_f(CH_2CF_2)_m-SO_2M \quad [2]$$

$$R_f(CH_2CF_2)_m-(CH_2)_{n'}SO_3M \quad [3]$$

in which:

- R_f is a linear or branched perfluoroalkyl group comprising from 1 to 5 carbon atoms, preferably from 2 to 4,
- m is an integer from 2 to 6,
- n is an integer from 0 to 2,
- n' is 0 or 2,
- M is a hydrogen atom or an alkali metal atom or an ammonium group or an ammonium group comprising at least one lower alkyl substituent.

2 Process according to Claim 1, in which M is ammonium.

3 Process according to either one of the preceding claims, in which R_f comprises from 2 to 4 carbon atoms.

4 Process according to any one of the preceding claims, in which m has the value 3, 4 or 5.

5 Process according to any one of the preceding claims, in which n has the value 0 or 1.

6 Process according to any one of the preceding claims, in which the surfactant is that of formula [1].

7 Process according to Claim 5, in which the surfactant is chosen from one or more of the following products:

$C_2F_5(CH_2CF_2)_3$-$CH_2CO_2NH_4$

$C_2F_5(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_2F_5(CH_2CF_2)_3$-CO_2NH_4

$C_2F_5(CH_2CF_2)_2$-CO_2NH_4

$C_3F_7(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_3F_7(CH_2CF_2)_3$-CO_2NH_4

$C_4F_9(CH_2CF_2)_3$-CO_2NH_4

$C_4F_9(CH_2CF_2)_2$-$CH_2CO_2NH_4$

$C_4F_9(CH_2CF_2)_2$-CO_2NH_4

$C_2F_5(CH_2CF_2)_3CH_2CH_2\ SO_3K$

$C_3F_7(CH_2CF_2)_2CH_2CH_2SO_3K$

$C_4F_9(CH_2CF_2)_3CH_2CH_2SO_3K$

$C_4F_9(CH_2CF_2)_2CH_2CH_2SO_3K$

8 Batchwise or semicontinuous process for the manufacture of fluoropolymer according to any one of the preceding claims, in which:

- water, the surfactant and optionally a paraffin wax are charged to the polymerization reactor,
- the reactor is deaerated to remove the oxygen,
- the reactor is brought to the chosen temperature and the fluoromonomer and optionally one (or more) optional comonomer(s) are charged until the desired pressure is reached,
- the optional transfer agent is introduced into the reactor, either in its entirety or partly at the start and partly during the polymerization,
- the initiator is added, in all or in part, to initiate the polymerization, and the fall in pressure which results therefrom is compensated for by the addition of fluoromonomer and optional comonomer,
- the possible remainder of the initiator is added during the polymerization,

- after introduction of the planned amount of fluoromonomer and optional comonomer, the reactor is degassed and the fluoropolymer is separated by any means from the water and possible residues of the reactants used.

9 Process according to any one of the preceding claims, in which the fluoropolymer is PVDF homopolymer or copolymer.

10 Products of following formula:

$$R_f(CH_2CF_2)_{m-1}-(CH_2)_nCO_2M \qquad [1]$$

in which:

- R_f is C_2F_5,
- m is an integer with the value 4 or 5,
- n is an integer from 0 to 2,
- M is a hydrogen atom or an alkali metal atom or an ammonium group or an ammonium group comprising at least one lower alkyl substituent.

11 Products of following formula:

$$R_f(CH_2CF_2)_mSO_2M \qquad [2]$$

$$R_f(CH_2CF_2)_m(CH_2)_{n'}SO_3M \qquad [3]$$

in which:

- R_f is a linear or branched perfluoroalkyl group comprising from 1 to 5 carbon atoms, preferably from 2 to 4,
- m is an integer from 3 to 6,
- n' is 0 or 2,
- M is a hydrogen atom or an alkali metal atom or an ammonium group or an ammonium group comprising at least one lower alkyl substituent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/007061

A. CLASSIFICATION OF SUBJECT MATTER
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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)
IPC 7 C11D C08F

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 02, 5 February 2003 (2003-02-05) & JP 2002 308914 A (DAIKIN IND LTD), 23 October 2002 (2002-10-23) abstract; claims 1-8	1-11
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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