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Process for preparing peroxidic perfluoropolyoxyalkylenes

Verfahren zur Herstellung von peroxiperfluoropolyxyalkylene

Procédé de préparation de perfluoropolyoxyalkylènes péroxidiques

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Proprietor: AUSIMONT S.p.A.
I-20121 Milano (IT)

Inventors:
• Marchionni, Giuseppe
Milano (IT)
• Guarda, Pier Antonio
Nole, Torino (IT)

Representative: Sama, Daniele, Dr. et al
Sama Patents,
Via G.B. Morgagni, 2
20129 Milano (IT)

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EP-A- 0 393 700
EP-A- 0 654 493
US-A- 3 847 978

EP-A- 0 393 705
EP-A- 0 695 775
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Description

[0001] The present invention relates to a process for preparing peroxidic perfluoropolyoxyalkylenes, usually called peroxidic perfluoropolyethers.

[0002] More particularly, it relates to a process for preparing peroxidic perfluoropolyethers obtained by oxidation of tetrafluoroethylene in the presence of solvents.

[0003] As known, peroxidic perfluoropolyethers are used as initiators of radical polymerizations and as curing agents for polymers. They can be transformed into inert perfluoropolyethers, i.e. devoid of peroxidic groups and reactive terminal groups, which are used as inert fluids in various applications: “testing” in electronics, vapour and liquid phase soldering, protection of building materials, lubrication, etc. Moreover, functional perfluoropolyethers, used for instance as intermediates for polymers, can be obtained from peroxidic perfluoropolyethers by means of known techniques of chemical reduction.


[0005] It is also known to carry out the reaction between tetrafluoroethylene and oxygen without using ultraviolet radiations, provided that a substance acting as polymerization initiator is present, said compound having one or more F-X bonds, wherein X is chosen from O and halogen. For Instance fluorine and hypofluorites up to 3 carbon atoms can be mentioned. See patents EP 0393700 and EP 0393705. According to the process described in these patents, by increasing the ratio between the amounts of monomer and initiator fed in the process, products with rising molecular weight are obtained. It has been noticed, however, that at the same time the content of peroxidic oxygen increases over the limit of acceptability, estimable around a peroxidic power value (PO), defined as grams of peroxidic oxygen per 100 g of product, equal to about 4, almost reaching the danger point set around 4.5-5. Perfluoropolyether products having number average molecular weight higher than 5000 and contemporaneously with a PO value lower than the maximum acceptability limit above mentioned cannot be obtained in the absence of ultraviolet radiation.

[0006] It is to be noticed that the problem of the molecular weight control and of the PO does not exist in the processes of perfluoroolefins photooxidation. It is indeed known that in the processes using ultraviolet radiations it is possible to obtain perfluoropolyethers with both molecular weight and PO independently controlled from each other. In particular peroxidic perfluoropolyethers with sufficiently high molecular weights and controlled PO can be obtained. Such polymers can be used for obtaining derivatives with a good functionality value \( f \geq 1.7 \), said functional derivatives being obtainable by chemical reduction and with molecular weight high enough to be of industrial interest.

[0007] Photooxidation processes have however the drawback due to the fact that their productivity is bound to the radiant power of the lamp. Therefore this implies high costs plants.

[0008] The oxidative process of the perfluoroolefins in the absence of UV radiations allows instead a high productivity and lower plant costs, but, as already said before, does not allow a simultaneous control of PO and of the molecular weight of the peroxidic perfluoropolyether and therefore of the characteristics of the functional derivatives obtainable therefrom.

[0009] From a previous European patent application in the name of the Applicant, EP-A-0 654 493, it is known that it is possible to utilize the oxidation process in the absence of radiations to obtain peroxidic perfluoropolyethers having high molecular weight and at the same time a controlled PO, by operating under pressure and with a molar ratio TFE/chemical initiator (for instance \( \text{F}_2 \)) higher than 33. In practice, by operating under pressure, in the absence of UV radiations, polymers having a lower number of peroxidic units are obtained, the other conditions being equal. It is thus possible to further increase the olefin flow-rate/initiator flow-rate ratio to increase the content of peroxidic units up to the extent obtainable at room pressure, with the final result to synthetize under pressure a polymer with higher molecular weight, the content of peroxidic units being equal, with respect to that obtainable at room pressure. It is therefore possible by operating at higher pressure to obtain polymers with average molecular weight higher and higher, the PO being equal. This fact is highly desirable for the reasons described in detail in the same European patent application EP-A-0 654 493 incorporated herein by reference, i.e. to be able to obtain functional derivatives (by chemical reduction of the peroxidic crude product) having a higher functionality, the molecular weight being equal.

[0010] The Applicant has unexpectedly and surprisingly found that it is possible to obtain peroxidic perfluoropolyethers having higher molecular weights, the PO being equal, by operating at the same temperature and working pressure of the former patent application mentioned above if one operates in the presence of a specific compound as defined hereunder. This allows moreover to obtain products similar to those obtainable at higher pressures, by operating at lower pressures, with all plant and safety advantages involved.

[0011] An object of the present invention is a tetrafluoroethylene oxidation process at temperatures comprised between -100°C and -40°C, preferably -90 and -60°C, in the absence of UV radiations and by operating in the presence of a chemical initiator containing at least one F-X bond, wherein X is oxygen or halogen, by operating with total pressures comprised between 0 and 15 relative bar and in the presence of a solvent comprising an amount of \( \text{COF}_2 \) higher than 8% by moles or in the presence of \( \text{COF}_2 \) alone. When X is oxygen, the...
F-X bonding is F-O-.

[0012] The chemical initiator is described in patent applications EP 393700 and EP 393705.

[0013] Preferably the chemical initiator is selected in the group formed by fluorine and by alkyl hypofluorites containing up to 3 carbon atoms.

[0014] The process of the present invention is carried out by feeding in the liquid phase, initially constituted by the solvent, a gaseous flow of oxygen and a gaseous flow of chemical initiator and a gaseous flow of tetrafluoroethylene. Sometimes also an inert gas, optionally mixed with the chemical initiator or with oxygen, is fed in the liquid phase. The inert gas, if used, is preferably selected from nitrogen, argon, helium, CF₃ and C₂F₆. A particular case of the use of nitrogen as inert gas is given by the use of air instead of oxygen.

[0015] The solvents utilized are those commonly indicated in the art for the TFE oxidation at low temperature, provided that they are liquid in the reaction conditions of the present invention.

[0016] The solvent is preferably selected from linear and cyclic fluorocarbons, optionally containing hydrocarbon and/or chlorine. Examples of preferred solvents are: CFCl₃, CF₂Cl₂, CF₂HCl, CF₃-CF₂H, CF₃H, CF₂H, CHClF-CF₃ and/or CHF₂-CClF₂ optionally in admixture with CH₂F₂F₂F⁻CF₃, CF₃CFHCF₂CF₃, CF₃CFHCF₃CF₆. Azeotropic or near-azeotropic mixtures of two or more of the mentioned compounds can also be employed. Other utilizable solvents are perfluoroolefins, perfluorocyclobutane, perfluorocyclohexane, chloropentafluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichlorotetrafluoroethane. Also perfluoroamines and perfluoroethers and polyethers, optionally containing hydrogen, can be used as solvent. Examples of this type are:

- CH₃OCF₂CFHCF₃
- C₆F₁₃-O-C₂F₄O-CF₂H
- C₈F₁₇-O-CF₂H
- C₇F₁₅-O-
- C₆F₁₃-O-C₂F₄O-CF₂H
- C₃F₇OCH₃
- C₂F₅OC₂H₅
- C₂F₅CFHCF₂H
- CHClF-CF₃ and/or CHF₂-CClF₂ optionally in admixture with CH₂F₂F₂F⁻CF₃, CF₃CFHCF₂CF₃, CF₃CFHCF₃CF₆.

[0017] The room pressure can be utilized or it is possible to operate under pressure as already indicated.

[0018] The chemical initiator, for instance fluorine, is fed in the liquid phase in amounts generally comprised between 0.001 and 0.1 by moles per hour per liter of liquid phase.

[0019] The TFE concentration in liquid phase generally ranges from 0.005 to 1 mole/l of solution, preferably from 0.01 to 0.5 moles/l.

[0020] The process can be carried out both in a discontinuous and, preferably, in a continuous way.

[0021] The feeding molar ratios TFE/chemical initiator are generally comprised between 10 and 200, preferably between 40-120.

[0022] The essential component of the present invention, COF₂, is prepared according to well known methods of the literature, see for instance Journal American Chemical Society, July 30, 1969, p. 4432-4436 M. Wechsberg and G. H. Cady.

[0023] Preferably the amount by moles of COF₂, when it is in admixture with the solvent, is comprised between 15 and 60%.

[0024] By the process of the present invention a peroxodic perfluropolyether is obtained having a lower PO than when one operates under the same temperature, reactants flow-rates (TFE and initiator), pressure conditions, but in the absence or in the presence of limited amounts of COF₂ in the reaction phase, outside the lower limit of the present invention. It is therefore possible to increase the ratio between olefin and initiator feeding so as to obtain a polymer with a PO equal to that obtained in the solvent not containing COF₂ or containing an amount by moles of COF₂ lower than the values of the present invention. The obtained result is therefore a polymer with higher molecular weight and PO equal to that obtainable in a solvent without COF₂, the other reaction conditions, such as temperature, pressure, reactor configuration and volume, being equal.

[0025] It has been found by the Applicant that a method to obtain COF₂ resides in recycling COF₂ formed as reaction by-product in the oxidation reaction up to the obtainment of the concentrations indicated above. By operating with a continuous plant, the obtained peroxodic polymer is recycled and the COF₂ is concentrated in the solvent up to the desired values.

[0026] In the processes of the art when one operates in a continuous way, the solvent and the unreacted perfluoroolefins are recycled after separation of the reaction-by-products. Unexpectedly the Applicant has found that one of the reaction by-products, COF₂, can be utilized according to the present invention to obtain the results described hereunder.

[0027] The peroxodic polymers obtained have the following general formula:

$$A-O(CF₂-CF₂-O)_{p}(CF₂-O)_{q}(O)⁻⁻B$$

wherein the terminals A and B can be equal to or different from each other and comprise -CF₂-X, -CF₂-CF₂X wherein X indicates a radical group deriving from the...
flow equal to 4.6 Nl/h (molar ratio TFE/F2 =48.7) are then introduced in an AISI reactor, with a capacity of about 25 l, equipped with a magnetic stirrer and gas feeding pipes, cooled at -80°C. 400 Nl/h of oxygen are fed under pressure and the reactor is pressurized (by means of a con- 

tractive purposes and are not limitative of the present inven-

[0031] The following examples are given for illustrative purposes and are not limitative of the present invention.

EXAMPLE 1

EXAMPLE 1A (comparative)

[0032] 20 l of dichlorodifluoromethane (R-12) are introduced in an AISI reactor, with a capacity of about 25 l, equipped with a magnetic stirrer and gas feeding pipes, cooled at -80°C. 400 Nl/h of oxygen are fed under pressure and the reactor is pressurized (by means of a con- 

tractive purposes and are not limitative of the present inven-

EXAMPLE 1B (comparative)

[0033] After 3 hours of reaction one starts to continuously run the plant of Ex. 1A: a flow of reaction mixture is extracted continuously from the reactor and sent to an evaporator, in which solvent and by-products are evaporated leaving the polymer which is continuously extracted. In this way the polymer concentration was kept constant for the whole test and equal to about 6% by weight. The solvent is separated by distillation of the by-products and recycled into the reactor. The reaction time in Ex. 1B was 2 hours.

EXAMPLE 1C (comparative)

[0034] After a total reaction time of 5 hours (always from the beginning of the reaction, i.e. 3 hours + 2 hours) the COF2 separated from the solvent instead of being eliminated as by-product, is condensed and added to the solvent and recycled in the reactor. From this moment the solvent is charged with COF2 produced and recycled in the reactor.

The reaction time in Ex. 1C was 7 hours.

EXAMPLE 1D (comparative)

[0035] After about 12 total hours of working the drawn polymer showed a content of peroxidic units (PO, expressed as g of active oxygen per 100 g of polymer) equal to 3.2.

The reaction time in Ex. 1D was 6 hours.

EXAMPLE 1E (comparative)

[0036] After 18 total hours of working the PO was equal to 2.97 and the 19F-NMR analysis indicated an average molecular weight equal to 6350 and a p/q ratio = 5.14 (the molecular weight determined by 19F-NMR analysis is a number average Mw).

EXAMPLE 1F

[0037] At such running time the gaschromatographic analysis of the reaction mixture gave a molar percentage of COF2 of 7%, of C2F4 of 0.3%, of C2F4O of 0.4% and of tetrafluoroethylene of 0.40%. The reaction time in Ex. 1E was 25 hours.

[0038] After 43 total hours of running the molar percentage of COF2 resulted equal to 16% (C2F6=0.3%, C2F4O=0.5%, TFE = 0.13%); the drawn polymer showed a PO of 1.51 and a number average molecular
weight of 6150 with p/q ratio = 2.07.
The reaction time in Ex. 1F was 3 hours.

EXAMPLE 1G

[0039] After 46 hours the TFE concentration was no longer gaschromatographically detectable. At 67 hours of running the reaction mixture analysis showed a content in COF_2 equal to 50% (C_2F_3O= 0.2%, TFE=0%) and the drawn polymer had a PO equal to 0.36 and a number average molecular weight of 5600 with p/q ratio = 0.09. The reaction time in Ex. 1G was 26 hours.

EXAMPLE 1H

[0040] After 72 hours of running the fluorine flow-rate was reduced to 3.55 Nl/h, rising thus the TFE/F_2 ratio to 63. In the following running hours, the content of COF_2 in the reaction mixture remained nearly constant around 55% by moles. Shortly afterwards the variation of the flow-rates, the TFE concentration was measurable again, around 0.3% molar. The polymer drawn after 76 total hours of running had a PO of 1.44 and a number average molecular weight of 7800 with p/q ratio of 1.45.

EXAMPLE 2

[0041] By utilizing the plant of Example 1, 20 l of dichlorodifluoromethane are introduced in the reactor at the temperature of -80°C. With the same procedure of that utilized in example 1, 600 Nl/h of oxygen, 336 Nl/h of tetrafluoroethylene (TFE) and 8.4 Nl/h of fluorine (TFE/F_2=40 molar ratio) are fed by maintaining the temperature of the reactor at -80°C and the pressure at 4 absolute bar.

After some hours of running one starts to extract a flow of reaction mixture which is sent to the evaporator, by recycling solvent and COF_2 and extracting the polymer so as to maintain constant around 7% by weight the polymer concentration in the reactor.

[0042] In these conditions of running the tetrafluoroethylene concentration is not detectable by gaschromatographic analysis and COF_2 accumulates in the time.

[0043] After 26 hours of running the COF_2 concentration in the reaction mixture is 45% molar. At this point the reactants flow-rates are set as follows: oxygen = 400 Nl/h, tetrafluoroethylene (TFE) = 224 Nl/h, fluorine = 3.4 Nl/h, (TFE/F_2=66 ratio). The plant is then carried out so as to maintain constant the COF_2 (around 47% molar) in the successive running hours, by recycling in the solvent only part of the COF_2 produced.

The tetrafluoroethylene concentration quickly reaches the value of 0.6% molar and maintains constant for the rest of the running.

[0044] A sample of the polymer extracted after 39 total hours of running shows a PO of 3.68, a number average molecular weight of 8700 amu with p/q ratio = 7.74.

EXAMPLE 3

[0045] By utilizing the plant of Example 1, 20 l of dichlorodifluoromethane are introduced in the reactor at the temperature of -80°C. With the same procedure of that utilized in example 1, 500 Nl/h of oxygen, 336 Nl/h of tetrafluoroethylene and 8.4 Nl/h of fluorine (TFE/F_2=40 molar ratio) are fed by maintaining the temperature of the reactor at -80°C and the pressure at 4 absolute bar.

After some hours of running one starts to extract a flow of the reaction mixture which is sent to the evaporator, by recycling solvent and COF_2 and extracting the polymer so as to maintain constant its concentration in the reactor mixture.

[0046] In these running conditions the tetrafluoroethylene concentration in the reaction mixture is not detectable by gaschromatographic analysis. A polymer with a very low PO is obtained and the by-product COF_2 which is produced accumulates progressively in the reaction mixture.

After 24 hours of running the COF_2 concentration in the reaction mixture is equal to 44% molar.

The feeding flow-rates are modified as follows: oxygen 400 Nl/h, tetrafluoroethylene 224 Nl/h, fluorine 3.3 Nl/h (TFE/F_2 ratio = 68); temperature and pressure are maintained at the values indicated above.

After a short time TFE is detectable at the gaschromatographic analysis and within a few hours it reaches a concentration equal to 0.5% molar; such concentration is kept for the successive 45 hours of the running. During this period of time the COF_2 concentration in the reaction mixture slowly increases up to a final value equal to 60% by moles.

[0047] The polymer produced shows a PO of 3.77 and a viscosity at 20°C equal to 830 cSt; the 19F-NMR shows a p/q ratio equal to 8.59, a number molecular weight of 9800.

EXAMPLE 3A (comparative)

[0048] In the reactor of example 1, 20 l of dichlorodifluoromethane were introduced at the temperature of -80°C. With the same procedure as that utilized in Example 1, 400 Nl/h of oxygen, 224 Nl/h of tetrafluoroethylene and 4.6 Nl/h of fluorine were fed, by keeping the temperature at -80°C and the pressure at 4 absolute bar for the whole test, equal to 5 hours and 40 minutes. The feeding molar ratio was equal to 48.7.

[0049] Unlike the previous examples the plant was carried out in batch, that is the flow of the reaction mixture was not extracted, wherefore the polymer accumulated during the reaction.

[0050] The olefin concentration ranged from an initial value of 0.24% by moles to a final concentration of 0.86% by moles and the one of COF_2 constantly rose in the time up to a final value of 7.5% by moles.

[0051] The polymer reached a final concentration in the reactor equal to 15% by weight. Such polymer
showed a PO of 2.72, a number average molecular weight equal to 6150 with p/q ratio = 3.41.

Claims

1. Tetrafluoroethylene oxidation process at temperatures comprised between -100°C and -40°C, in the absence of UV radiations, and by operating in the presence of a chemical initiator containing at least one F-X bond, wherein X is oxygen or halogen, by operating with total pressures comprised between 0 and 15 relative bar and in the presence of a solvent comprising an amount of COF₂ higher than 8% by moles or in the presence of COF₂ alone.

2. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 1, wherein the temperature is comprised between -90 and -60°C.

3. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-2, wherein the chemical initiator is chosen from fluoride and alkyl hypofluorites containing up to 3 carbon atoms.

4. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-3, wherein the solvent is selected from linear and cyclic fluorocarbons, optionally containing hydrogen and/or chlorine; perfluoropropane, perfluorocyclobutane, perfluorocyclohexane, chloropentafluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichlorotetrafluoroethane; perfluoroamines and perfluoroethers and polyethers, optionally containing hydrogen.

5. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 4, wherein the solvent is selected from: CFCl₃, CF₂Cl₂, CF₂HCl, CF₂CF₂H, CF₂H₂CF₂H, CF₂H₂CF₂H, CH₂=CF₂ and/or CHF₂-CCl₂F, CF₃CFHCF₂CF₃, CF₃CFHCFHCF₂CF₃ or azeotropic or near-azeotropic mixtures of two or more of the cited compounds; CH₃OCH₂, CF₃CFHCF₂CF₃, C₈F₁₇-O-C₂F₄H, C₈F₁₇-O-C₂F₄H, C₁₂F₂₅-O-C₂F₄H, C₁₆F₃₃-O-C₂F₄H, C₂₀F₄₁-O-C₂F₄H, C₂⁴F₅₃-O-C₂F₄H, F(CH₂-CF₂-C₂F₄-O)nCF₂CF₂H with X=F, and n being an integer from 0 to 4, extremes included, and T-O(C₃F₆O)ₚ₀(C₂F₄O)ₚ₁(CF₂O)ₚ₂(O)ₚ₃, where p, q and r indexes equal to or different from each other are integers, the sum p+q is an integer between 2 and 1000, the p/q ratio is comprised between 0.1 and 40, the r/(p+q) ratio is comprised between 0.01-0.3.

6. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-5, wherein the chemical initiator is fed in the liquid phase in amounts comprised between 0.001 and 0.1 moles per hour per liter of liquid phase; the TFE concentration in liquid phase ranges from 0.005 and 1 mole/l of solution.

7. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 6, wherein in the feeding molar ratios TFE/chemical initiator are comprised between 10 and 200.

8. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 7, wherein the amount by moles of COF₂ in the solvent is comprised between 15 and 60%.

9. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-8, wherein the obtained peroxidic polymers have the following general formula:

A-O-(CF₂-CF₂-O)ₚ-(CF₂-O)ₚ₁-(O)ₚ₂-(CF₂-CF₂-O)ₚ₃-B

wherein the terminals A and B can be equal to or different from each other and comprise -CF₂X, -CF₂-CF₂-X, wherein X indicates a radicalic group deriving from the kind of initiator utilized; the p, q and r indexes equal to or different from each other are integers, the sum p+q is an integer between 2 and 1000, the p/q ratio is comprised between 0.1 and 40, the r/(p+q) ratio is comprised between 0.01-0.3.

10. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-9, wherein COF₂ comes from the recycle of the COF₂ by-product formed in the oxidation reaction till obtaining of the concentrations of claim 1.

11. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 1-10, wherein peroxidic perfluoropolyethers are trans-

12. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 11, wherein in the peroxidic polymer p+q is comprised between 10 and 500, the p/q ratio is comprised between 0.2 and 20.

13. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claims 11-12, wherein peroxidic perfluoropolyethers are trans-

14. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 12, wherein the obtained peroxidic polymers have the following general formula:

A-O-(CF₂-CF₂-O)ₚ-(CF₂-O)ₚ₁-(O)ₚ₂-(CF₂-CF₂-O)ₚ₃-B

wherein the terminals A and B can be equal to or different from each other and comprise -CF₂X, -CF₂-CF₂-X, wherein X indicates a radicalic group deriving from the kind of initiator utilized; the p, q and r indexes equal to or different from each other are integers, the sum p+q is an integer between 2 and 1000, the p/q ratio is comprised between 0.1 and 40, the r/(p+q) ratio is comprised between 0.01-0.3.
formed into products without peroxidic oxygen by a thermal treatment at temperatures comprised between 100-250°C or by UV radiations, in the presence or not of solvents.

14. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 13, wherein the obtained polymer is submitted to fluorination treatment to obtain perfluropolyether with perfluoroalkyl terminals.

15. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 13, wherein the obtained polymer is submitted to chemical reduction and to subsequent transformation reactions to obtain functional products.

16. Tetrafluoroethylene oxidation process in the absence of UV radiations, according to claim 15, wherein the functional derivative is in the form of carboxylic acid salt, optionally subjected to decarboxylation processes in the presence of hydrogen-donor substances to obtain perfluropolyethers having both terminals -OCF₂H.

Patentansprüche

1. Verfahren zur Oxidation von Tetrafluorethylen bei Temperaturen zwischen -100°C und -40°C in Abwesenheit von UV-Strahlung, das in Anwesenheit eines chemischen Initiators, der mindestens eine F-X-Bindung enthält, worin X Sauerstoff oder Halogen ist, durchgeführt wird und das bei Gesamtdrücken zwischen 0 und 15 relativen Bar und in Anwesenheit eines Lösungsmittels, umfassend eine COF₂-Menge von mehr als 8 Mol-%, in Anwesenheit von COF₂ allein, durchgeführt wird.

2. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach Anspruch 1, worin die Temperatur zwischen -90 und -60°C beträgt.

3. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 2, worin der chemische Initiator ausgewählt ist aus Fluor und Alkylhypofluoriten mit bis zu 3 Kohlenstoffatomen.

4. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 3, worin das Lösungsmittel ausgewählt ist aus linearen und cyclischen Fluorkohlenstoffen, die gegebenenfalls Wasserstoff und/oder Chlor enthalten; Perfluoropropan, Perfluorocyclobutan, Perfluorcyclohexan, Chlorperfluorathyran, 1,1,2-Trichlor-1,2,2-trifluorethan, 1,2-Dichlortrifluorethan; Perfluoraminen und Perfluorethen und polyether, die gegebenenfalls Wasserstoff enthalten.

5. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach Anspruch 4, worin das Lösungsmittel ausgewählt wird aus: CFCl₃, CF₂Cl₂, CF₃HCl, CF₂-CF₂H, CF₃-CFH₂, CF₃H-CF₂H, CHClF-CF₃ und/ oder CHF₂-CClF₂, gegebenenfalls gemischt mit CHF₂-CH₂F, CF₃CFHCF₂CF₃, CF₃CFHCFHCF₂CF₃ oder azetropen oder nahezu azetropen Mischungen von zwei oder mehr der genannten Verbindungen; CH₃OCF₂CFHCF₃, C₂F₅-O-C₂F₄H, CF₂H-O-CF₂H, C₆F₅-O-C₂F₄H, C₆F₅-O-C₂F₄H, C₆F₅-O-C₂F₄H, C₆F₅-O-C₂F₄H, C₆F₅OCCH₁₃, C₄F₃OC₂H₅, C₃F₇OC₂H₅, C₃F₇OC₂H₅, C₃F₇OC₂H₅, F(CF₂-CF₂-CX'O)ₙCF₂CF₂H, worin X' = F, H und n eine ganze Zahl von 0 bis 4 ist, einschließlich der Grenzwerte, und T₀(C₂F₅O)ₚ₀(CF₂O)ₚ₀(CF₂O)ₚ₀-T, worin p₀, q₀ und r₀ ganze Zahlen von 0 bis 3 sind, einschließlich der Grenzwerte, und T und T* gleich oder voneinander verschieden sind und ausgewählt sind aus CF₃, C₂F₅, C₃F₇, CF₃H und CF₃CFH, CF₂CF₂H, wobei die Perfluoroxalkylen-Einheiten statistisch in der Polymerkette verteilt sind.

6. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 5, worin der chemische Initiator der flüssigen Phase in Mengen zwischen 0,001 und 0,1 Mol pro Stunde pro Liter flüssiger Phase zugeführt wird; und die TFE-Konzentration in flüssiger Phase im Bereich zwischen 0,005 und 1 Mol/l Lösung liegt.

7. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach Anspruch 6, worin die molaren Beschichtungsverhältnisse TFE/chemischer Initiator zwischen 10 und 200 betragen.

8. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach Anspruch 7, worin die molaren Beschichtungsverhältnisse TFE/chemischer Initiator zwischen 40 und 120 betragen.

9. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 8, worin die Molmenge an COF₂ im Lösungsmittel zwischen 15 und 60% beträgt.

10. Verfahren zur Oxidation von Tetrafluorethylen in Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 9, worin COF₂ aus dem Kreislauf des Nebenprodukts-COF₂ stammt, das in der Oxidationsreaktion gebildet wird, bis die Konzentrationen von Anspruch 1 erhalten werden.

11. Verfahren zur Oxidation von Tetrafluorethylen in
Abwesenheit von UV-Strahlung nach den Ansprüchen 1 bis 10, worin die erhaltenen peroxidischen Polymere die folgende allgemeine Formel aufweisen:

\[ A-O-(CF_2-CF_2-O)_p-(CF_2-O)_q-(O)r-B \]

worin die Enden A und B gleich oder verschieden voneinander sein können und \(-CF_2X, -CF_2-CF_2X\) umfassen, worin X eine Restgruppe darstellt, die von dem eingesetzten InitiatorTyp abgeleitet ist; die Indices p, q und r gleich oder voneinander verschieden ganze Zahlen sind, die Summe p + q eine ganze Zahl zwischen 2 und 100 ist, das p/q-Verhältnis zwischen 0,1 und 40 ist und das r/(p+q)-Verhältnis zwischen 0,01 und 0,3 ist.

12. Verfahren zur Oxidation von Tetrafluorethen in Abwesenheit von UV-Strahlung nach Anspruch 11, worin das peroxidische Polymer p + q zwischen 10 und 500 und das p/q-Verhältnis zwischen 0,2 und 20 sind.

13. Verfahren zur Oxidation von Tetrafluorethen in Abwesenheit von UV-Strahlung nach Ansprüchen 11 bis 12, worin das peroxidische Perfluoropolyether durch eine thermische Behandlung bei Temperaturen zwischen 100 und 250°C oder durch UV-Strahlung in Anwesenheit oder Abwesenheit von Lösungsmitteln in Produkte ohne Peroxid-Sauerstoff überführt werden.

14. Verfahren zur Oxidation von Tetrafluorethen in Abwesenheit von UV-Strahlung nach Anspruch 13, worin das erhaltene Polymer einer Fluorierungsbehandlung unterworfen wird, um Perfluoropolyether mit Perfluoralkyl-Endgruppen zu erhalten.

15. Verfahren zur Oxidation von Tetrafluorethen in Abwesenheit von UV-Strahlung nach Anspruch 13, worin das erhaltene Polymer einer chemischen Reduktion und anschließenden Transformationsreaktionen unterworfen wird, um funktionelle Produkte zu erhalten.

16. Verfahren zur Oxidation von Tetrafluorethen in Abwesenheit von UV-Strahlung nach Anspruch 15, worin das funktionelle Derivat in Form eines Carbonsäuresalzes vorliegt, das gegebenenfalls De-carboxylierungsprozessen in Anwesenheit von Wasserstoff-Donor-Substanzen unterworfen wird, um Perfluoropolyether mit -OCF₂H an beiden Enden zu erhalten.

Revendications

1. Procédé d’oxydation du tétrafluoréthylène à des températures comprises entre -100 et -40°C, en l’absence de rayonnements UV, et en opérant en présence d’un amorceur chimique contenant au moins une liaison F-X, où X est un oxygène ou un halogène, en opérant sous des pressions totales comprises entre 0 et 15 bars relatifs, et en présence d’un solvant comprenant une quantité de COF₂ supérieure à 8 % en moles, ou en présence de COF₂ seul.

2. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 1, dans lequel la température est comprise entre -90 et -60°C.

3. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-2, dans lequel l’amorceur chimique est choisi parmi le fluor et les hypofluorites d’alkyle ayant jusqu’à 3 atomes de carbone.

4. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-3, dans lequel le solvant est choisi parmi les fluorocarbures linéaires et cycliques, contenant éventuellement de l’hydrogène et/ou du chlore ; le perfluoropropane, le perfluorocyclobutane, le perfluorocyclohexane, le chloropentafluoréthane, le 1,1,2-trichloro-1,2,2-trifluoréthane, le 1,2-dichlorotétrafluoréthane, les perfluoraminés et les perfluoréthers et les polyéthers, contenant éventuellement de l’hydrogène.

5. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 4, dans lequel le solvant est choisi parmi CFCl₃, CF₂Cl₂, CF₂HCl, CF₂-CF₂H, CF₃-CF₂H, CF₂H-CF₂H, CH₂F-CF₂F, et/ou CH₂F-CF₂F éventuellement en mélange avec CH₂F-CF₂F, CF₂CFCH₂CF₃, CF₃CFHCFCH₂CF₃ ou des mélanges azéotropiques ou pseudoazéotropiques de deux ou plus des composés cités ; CH₃OCF₂CFHCF₃, C₂F₅OCF₂CF₂OC₂H₄, C₂H₅OC₂H₄CF₂H, C₆H₁₃OC₂H₄CF₂H, C₆H₁₃OC₂H₄CF₂H, C₂F₅OC₂H₄CF₂H, C₄F₉OC₂H₄F, C₆F₁₃OC₂H₄F, C₂F₅OC₂H₄CF₂H, F(C₂F₂-CF₂-CF₂O)nCF₂CF₂H, avec X = F, H, et n étant un entier de 0 à 4, limites comprises, et T-O(C₃F₆O)pO(C₂F₄O)qO(CF₂O)rO-T' où po, qo et ro sont des entiers de 0 à 3, limites comprises, et T et T', identiques ou différents l’un de l’autre, sont choisis parmi CF₃, CF₂CF₃, C₇F₁₅O-C₂F₄H, C₄F₉OCH₃, C₃F₇OCH₃, C₂F₅OCH₃, F(C₂F₂-CF₂-CX'O)nCF₂CF₂H, avec X' = F, H, et n étant un entier de 0 à 4, limites comprises, et T-O(C₃F₆O)pO(C₂F₄O)qO(CF₂O)rO-T'o où po, qo et ro sont des entiers de 0 à 3, limites comprises, et T' et T'', identiques ou différents l’un de l’autre, sont choisis parmi CF₃, CF₂CF₃, C₇F₁₅O-C₂F₄H, C₄F₉OCH₃, C₃F₇OCH₃, C₂F₅OCH₃, F(C₂F₂-CF₂-CX'O)nCF₂CF₂H, les motifs perfluoroxyalkylène étant répartis au hasard dans la chaîne polymère.
6. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-5, dans lequel l’amorceur chimique est introduit dans la phase liquide en des quantités comprises entre 0,001 et 0,1 mole par heure par litre de phase liquide ; la concentration du TFE dans la phase liquide est comprise entre 0,005 et 1 mole par litre de solution.

7. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 6, dans lequel le rapport en moles entre le TFE et l’amorceur chimique de la charge est compris entre 10 et 200.

8. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 7, dans lequel le rapport en moles du TFE à l’amorceur chimique de la charge est compris entre 40 et 120.

9. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-8, dans lequel la quantité en moles de COF₂ dans le solvant est comprise entre 15 et 60 %.

10. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-9, dans lequel le polymère obtenu est soumis à un traitement de fluoration pour donner un perfluoropolyéther ayant des radicaux terminaux perfluoralkyle.

11. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon les revendications 1-10, dans lequel les polymères peroxydés obtenus ont la formule générale suivante :

  \[ A-O-(CF₂-CF₂-O)ₚ-(CF₂-O)ₚ-(O)ₚ-B \]

dans laquelle les radicaux terminaux A et B peuvent être identiques ou différents l’un de l’autre et comprennent -CF₂X,-CF₂-CF₂X, où X indique un groupe radicaire qui dérive de l’espèce d’amorceur utilisée ; les indices p, q et r, qui sont identiques ou différents les uns des autres, sont des entiers, la somme p + q est un entier de 2 à 1000, le rapport p/q est compris entre 0,1 et 40, le rapport r/(p+q) est compris entre 0,01 et 0,3.

12. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 11, dans lequel, dans le polymère peroxydé, p+q est compris entre 10 et 500, le rapport p/q est compris entre 0,2 et 20.

13. Procédé d’oxydation du tétrafluoréthylène en l’ab- sence de rayonnements UV selon les revendications 11-12, dans lequel les perfluoropolyéthers peroxydés sont transformés en produits sans oxygène de type peroxyde par un traitement thermique à des températures comprises entre 100 et 250°C ou par des rayonnements UV, en présence ou en l’absence de solvants.

14. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 13, dans lequel le polymère obtenu est soumis à une réduction chimique et à des réactions de transformations ultérieures pour donner des produits fonctionnels.

15. Procédé d’oxydation du tétrafluoréthylène en l’absence de rayonnements UV selon la revendication 13, dans lequel le dérivé fonctionnel se présente sous forme d’un sel d’un acide carboxylique, éventuellement soumis à des procédés de décarboxylation en présence de substances donneuses d’hydrogène, pour donner des perfluoropolyéthers ayant des radicaux terminaux -OCF₂H.