



(11) **EP 1 658 278 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
31.03.2010 Bulletin 2010/13

(21) Application number: **04772815.9**

(22) Date of filing: **30.08.2004**

(51) Int Cl.:
C07D 317/06^(2006.01) C07D 317/16^(2006.01)

(86) International application number:
PCT/JP2004/012866

(87) International publication number:
WO 2005/021526 (10.03.2005 Gazette 2005/10)

(54) **METHOD FOR PRODUCING FLUORINATED 1,3-DIOXOLANE COMPOUNDS, FLUORINATED 1,3-DIOXOLANE COMPOUNDS, FLUORINATED POLYMERS OF THE FLUORINATED 1,3-DIOXOLANE COMPOUNDS, AND OPTICAL OR ELECTRICAL MATERIALS USING THE POLYMERS**

VERFAHREN ZUR HERSTELLUNG VON FLUORIERTEN 1,3-DOXOLANVERBINDUNGEN, FLUORIERTEN 1,3-DIOXOLANEVERBINDUNGEN, FLUORIERTE POLYMERE VON DEN FLUORIERTEN 1,3-DIOXOLANE, UND VON OPTISCHEN UND ELEKTRISCHEN MATERIALIEN UNTER VERWENDUNG VON DIESEN POLYMEREN

PROCEDE POUR COMPOSES FLUORES, COMPOSES FLUORES PRODUITS SUIVANT CE PROCEDE, POLYMERES FLUORES DES COMPOSES FLUORES, ET MATERIAUX OPTIQUES OU ELECTRIQUES UTILISANT CES POLYMERES

(84) Designated Contracting States:
BE DE FR GB IT

(30) Priority: **29.08.2003 US 498689 P**
15.06.2004 JP 2004177125

(43) Date of publication of application:
24.05.2006 Bulletin 2006/21

(60) Divisional application:
09006883.4 / 2 107 056

(73) Proprietor: **Japan Science and Technology Agency**
Kawaguchi-shi,
Saitama 332-0012 (JP)

(72) Inventors:

- **OKAMOTO, Yoshiyuki**
Fort Lee, NJ 07024-6705 (US)

• **KOIKE, Yasuhiro**
Yokohama-shi,
Kanagawa 225-0024 (JP)

(74) Representative: **Fuhlendorf, Jörn**
Dreiss Patentanwälte
Postfach 10 37 62
70032 Stuttgart (DE)

(56) References cited:
CA-A- 2 464 643 JP-A- 5 213 929
JP-A- 5 339 255 US-A- 3 308 107
US-A- 3 450 716

• **WEIHONG LIUM YASUHIRO KOIKE, YOSHI OKAMATO: "Synthesis and Characterisation of Poly(perfluoro-2-methylene-1,3-dioxolane)" POLYMER PREPRINTS, vol. 45, no. 2, 2004, pages 663-664, XP009046256**

EP 1 658 278 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

BACKGROUND OF THE INVENTION

5 Technical Field

[0001] The present invention relates to a method for fluorinated compounds, fluorinated compounds produced by the method, fluorinated polymers obtained from the fluorinated compounds, and optical or electrical materials using the fluorinated polymers.

10

Related Art

[0002] Fluorinated polymers are useful materials that are used in various applications, for example, plastic optical fibers and photoresist materials, or surface modifiers. However, the synthetic processes of fluorinated polymers are complicated and costly.

15

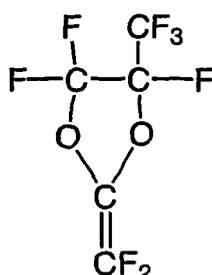
[0003] A fluorinated polymer is obtained by polymerization of a fluorinated compound having a polymeric unsaturated group. As an example of fluorinated polymers, 1,3-dioxolane derivatives and the like are disclosed in U.S. Patent No. 3,308,107, U.S. Patent No. 3,450,716; Izvestiya A Kademii Nank SSSR, Seriya Khimicheskaya, pp. 392-395, Feb 1988 by V.S. Yuminov et al. and pp/938-, April 1989 by V.S. Yuminov et al; and the like.

20

[0004] However, 1,3-dioxolane derivatives that have been conventionally known are limited to the structures of a compound represented by the following formula (A) disclosed in U.S. Patent No. 3,978,030, a compound represented by the following formula (B) disclosed in JP-A No. 5-339255, and the like. In these compounds, only a specific substitutional group can be located at a specified site on a five-membered ring of dioxolane.

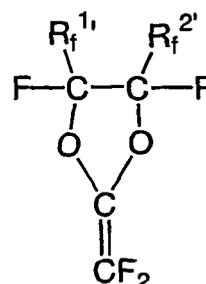
25

Formula (A)



30

Formula (B)



35

[0005] In Formula (B), $R_f^{1'}$ and $R_f^{2'}$ each independently represent a polyfluoroalkyl group having 1 to 7 carbon atoms.

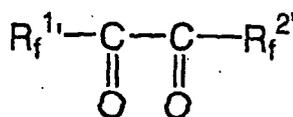
40

[0006] Such structural limitation results from the synthetic processes employed to form the polymers. For example, in a conventional method for synthesis of the compound represented by the above formula (A), only one fluorine-containing group may be located on a 1,3-dioxolane ring, and the fluorine-containing group that can be introduced is limited to a trifluoroalkyl group. In a conventional method for synthesis of the compound represented by the above formula (B), one polyfluoroalkyl group that can be introduced into a 1,3-dioxolane ring is located at each site of 4- and 5-membered rings, that is, the number of polyfluoroalkyl group is inevitably limited to two in total. Further, a material used for synthesizing the fluorinated compound represented by formula (B) is a compound represented by the following formula (C), and it is difficult to synthesize such compound.

45

50

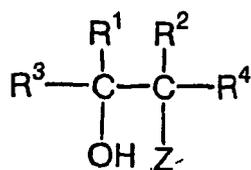
Formula (C)



55

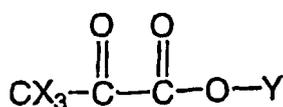
[0007] JP-A 05 213929 describes a process for the preparation of compounds of perfluoro 2-methylene-1,3-dioxolane,

but without of a compound of formula (2)



Formula (2)

[0008] Document CA-A2 464 643 discloses a reaction wherein compound a C(OH)-C(OH) moiety is reacted with a carbonyl containing compound to give 1,3-dioxolane compound, which is subsequently fluorinated and through two steps converted to the 2-divluoromethylene derivate. The document does not disclose the use of a compound of formular (1)



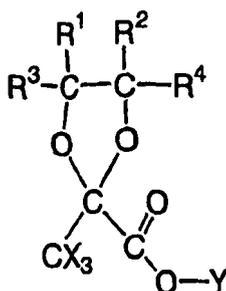
Formula (1)

containing the C(O)-OY moiety in a reaction with a compound containing the C(OH)-C(OH) moiety.

SUMMARY OF THE INVENTION

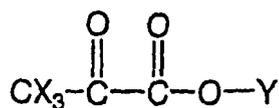
[0009] The present inventors have developed the following synthetic methods, therefrom have derived useful and novel fluorinated compounds, and optical or electrical materials using the polymers. The present invention will be described below.

[0010] A first aspect of the present invention is a method for producing a fluorinated compound represented by the following formula (3), the method comprising a step of obtaining the compound of the following formula (5)

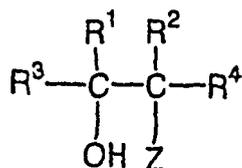


Formula (5)

wherein, in formula (5) X represents a hydrogen atom or a fluorine atom, Y represents a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, by fluorinating, in a fluorine-based solution under a fluorine gas atmosphere, a compound obtained by reacting at least one of kind of compound represented by the following formula (1) and at least one kind of compound represented by the following formula (2):

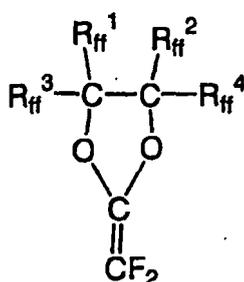


Formula (1)



Formula (2)

wherein in formula (1), X represents a hydrogen atom or a fluorine atom, and Y represents an alkyl group having 1 to 7 carbon atoms or a polyfluoroalkyl group having 1 to 7 carbon atoms; and in formula (2), Z represents a hydroxyl group, a chlorine atom, or a bromine atom, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms or a polyfluoroalkyl group having 1 to 7 carbon atoms.



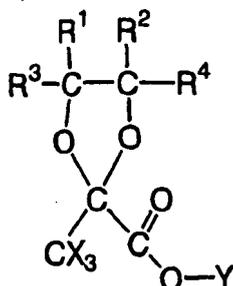
Formula (3)

[0011] Wherein, in formula (3), R_{ff}¹ to R_{ff}⁴ each independently represent a fluorine atom or a perfluoroalkyl group having 1 to 7 carbon atoms.

[0012] A second aspect of the present invention is the method for producing a fluorinated compounds according to the first aspect, wherein the fluorine gas atmosphere is a mixed atmosphere of nitrogen gas and fluorine gas, and a proportion of the nitrogen gas with respect to the fluorine gas is in a range from 2 to 4.

[0013] A third aspect of the present invention is the method for producing a fluorinated compounds according to the first aspect, wherein, in the step of fluorinating, a reaction temperature is kept in a range of 0 to 5°C, and stirring is carried out

[0014] A fourth aspect of the present invention is a compound represented by the following formula (5):



Formula (5)

wherein, in formula (5) X represents a hydrogen atom or a fluorine atom, Y represents a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

- 5 Fig. 1 is a graph showing refractive indexes of polymers synthesized by Examples 2 and 4.
 Fig. 2 is a graph showing the material dispersion of the polymer synthesized by Example 2.
 Fig. 3 is a graph showing the optical transmission of the polymer synthesized by Example 4.

DETAILED DESCRIPTION OF THE INVENTION

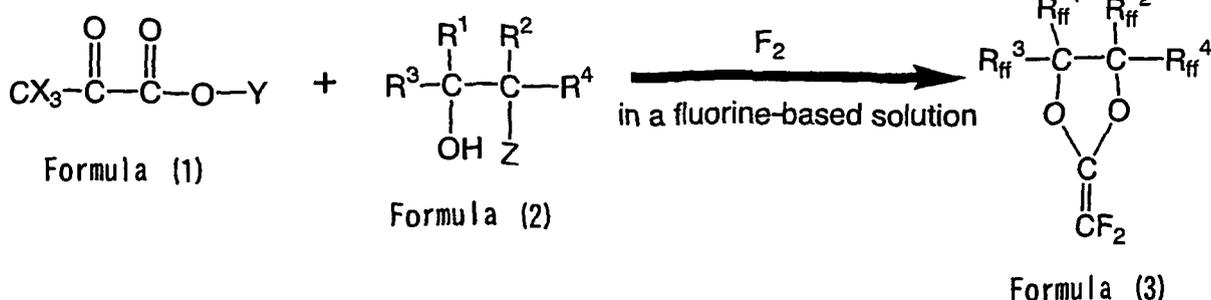
10

1. Method for producing fluorinated compounds

[0016] A description will be given of a method for producing fluorinated compounds, that are 1,3-dioxolane derivatives, according to the present invention.

- 15 **[0017]** In the production method of the present invention, a fluorinated compound that uses 1,3-dioxolane derivatives, represented by the following formula (3), is produced using the following formulae (1) and (2) in a fluorine-based solution in a flow of fluorine gas.

20



30

[0018] In Formula (1), X represents a hydrogen atom or a fluorine atom. From the viewpoint of ready availability, X is preferably a hydrogen atom. Y represents an alkyl group having 1 to 7 carbon atoms, preferably 1 to 3 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, preferably 1 to 3 carbon atoms, more preferably a perfluoroalkyl group having 1 to 3 carbon atoms.

35

Specially preferably, Y represents an alkyl group having 1 to 3 carbon atoms

[0019] In Formula (2), Z represents a hydroxyl group, chlorine atom, or bromine atom.

[0020] In Formula (2), R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms. After the compound represented by Formula (1) and the compound represented by Formula (2) are made to react with each other, hydrogen atoms that form a product are all fluorinated. Therefore R¹ to R⁴ may be hydrogen atom, alkyl group, or polyfluoroalkyl group. More preferably, R¹ to R⁴ each independently represent a hydrogen atom, or an alkyl group having 1 to 7 carbon atom because of cost-effective. Specifically preferably, R¹ to R⁴ each independently represent a hydrogen atom, or an alkyl group having 1 to 3 carbon atom. R¹ and R² may be bonded to each other to form a ring.

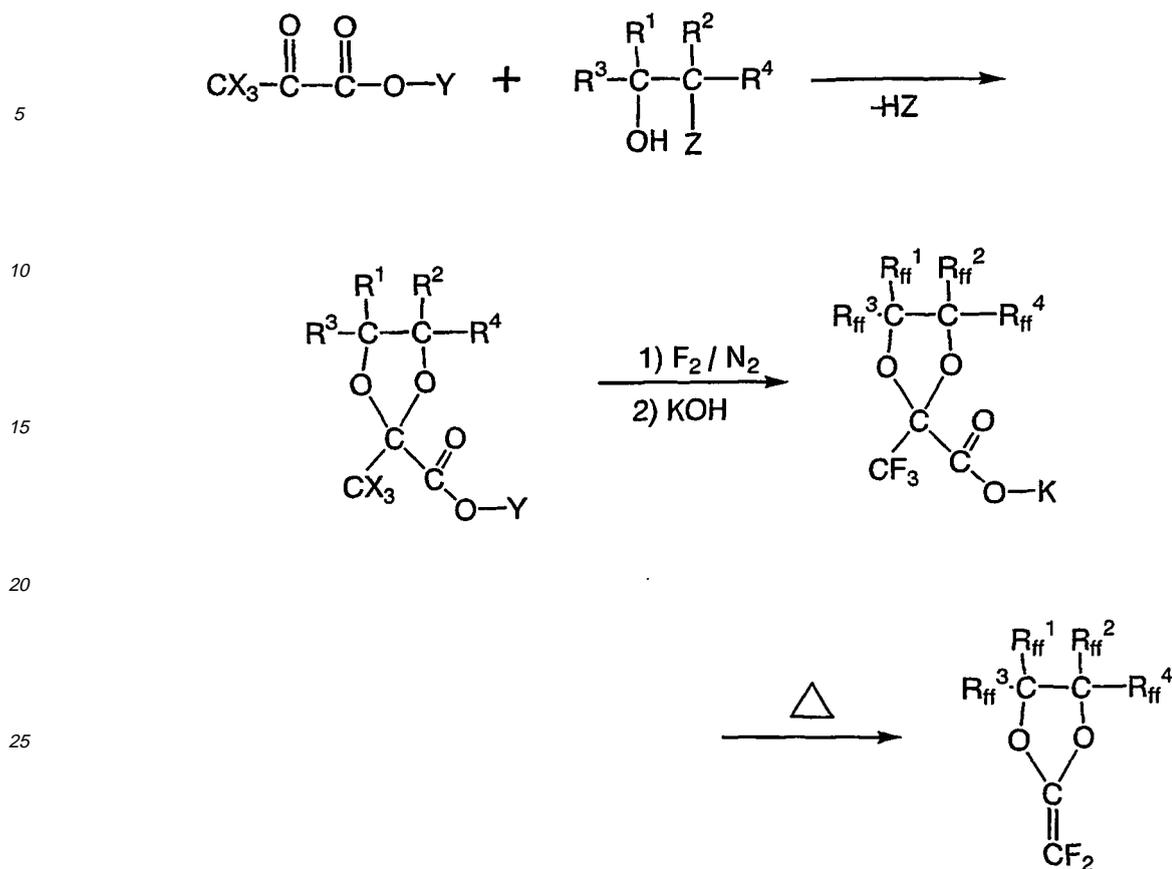
40

[0021] In Formula (3), R_{ff}¹ to R_{ff}⁴ each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 7 carbon atoms. Preferably, R_{ff}¹ to R_{ff}⁴ each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 3 carbon atoms. R_{ff}¹ and R_{ff}⁴ may be bonded to each other to form a ring.

[0022] Reaction schemes of these compounds are exemplified below, but the present invention is not limited to the same.

50

55



[0023] The production process of the present invention is broadly divided into, preferably, at least four steps as below.

- 35
- (1) a step in which the compound represented by the above formula (1) and the compound represented by the above formula (2) are made to undergo dehydration or dehydro halogenation reaction;
 - (2) a step in which the above compounds are fluorinated in a fluorine-based solution;
 - (3) a step in which a carboxylate salt is produced by a base; and
 - (4) a step of heating in order to decarboxylate the obtained carboxylate salt.

40 [0024] These four steps (1) to (4) will be described below in detail.

Step (1):

45 [0025] It is preferable that the compound represented by Formula (1) and the compound represented by Formula (2) are made to react with each other at an equimolar ratio. The compounds represented by Formula (1) may be used either singly or in combination of two or more. Further, the compounds represented by Formula (2) may be used either singly or in combination of two or more.

50 [0026] Moreover, since the above is an exothermic reaction, these compounds are preferably made to react with each other while being cooled. Other reaction conditions are not particularly limited, and prior to the subsequent step (2), a purification process such as distillation is also preferably added.

Step (2):

55 [0027] In this step, hydrogen atoms of the compound prepared by the step (1) are all substituted with fluorine atoms. To that end, preferably, the hydrogen atoms are directly fluorinated in a fluorine-based solution. As for such direct fluorination, refer to Synthetic Fluorine Chemistry, Eds by G.A. Olah, R.D. Chambers, and G.K.S. Prakash, J.Wiley and Sons. Inc. New York (1992), by R.J.Lagow, T.R.Bierschenk, T.J.Juhlke and H.kawa, Chapter 5: Polyether Synthetic Method.

EP 1 658 278 B1

[0028] The fluorine-based solution is not particularly limited. For example, 1,1,2-trichlorotrifluoroethane, polyfluorobenzene, and the like are preferable. Specific examples thereof include Fluorinert FC-75, FC - 77, FC - 88 (produced by 3M Corporation), and the like. The ratio of fluorine-based solution to the compound prepared by the step (1) is 2-10 times (mass ratio), more preferably, the ratio is 3-4 times.

[0029] The fluorination is carried with fluorine gas diluted with nitrogen gas. The ratio of nitrogen gas to fluorine gas is preferably 2-6 times (volume ratio), more preferably, the ratio is 2-4 times larger than fluorine gas.

[0030] The compound obtained through the step(1) is dissolved in the fluorine-based solvent (the weight ratio of the compound to the solution is 0.40-0.50). The solution is added slowly into the fluorine-based solution under F_2/N_2 stream. The addition rate is preferably 0.3ml/min. to 20ml/min., more preferably 0.5ml/min. to 10ml/min.

[0031] The reaction of the step(2) is carried out by controlling temperature. The reaction temperature should be under 5°C, preferably at between 0°C and 5°C. During step(2), the solution is preferably well stirred.

Step (3):

[0032] A carboxylate salt is produced from the fluorine compound obtained by step (2) by a base. As the base, potassium hydroxide, sodium hydroxide, cesium hydroxide, and the like are preferable. Potassium hydroxide is more preferable.

Step (4) :

[0033] The obtained carboxylate salt is heated and decarboxylated.

The heating temperature is preferably in the range of 250 °C to 320 °C, and more preferably in the range of 270 °C to 290 °C.

[0034] In the production method of the present invention, other steps in addition to the above steps (1) to (4) can be added.

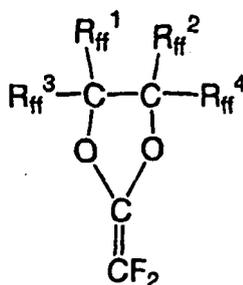
2. Method for producing fluorinated polymers

[0035] The above fluorinated compound undergoes radical polymerization in accordance with an ordinary method, thereby allowing production of a fluorinated polymer. A peroxide is preferably used as a radical catalyst, but in order that a fluorine atom of the fluorine compound may not be substituted with a hydrogen atom, a perfluoroperoxide is used.

3. Fluorinated compound

[0036] In the production method of the present invention, a hydrogen atom can be substituted with a perfluoro group or a fluorine atom at an arbitrary site on a 1,3-dioxolane ring, and perfluoro-2-methylene-1,3-dioxolane represented by the following formula (3) can be obtained.

Formula (3)



[0037] In Formula (3), R_{ff}^1 to R_{ff}^4 each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 7 carbon atoms.

Preferably, R_{ff}^1 to R_{ff}^4 each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 3 carbon atoms.

[0038] The compound represented by Formula (3) can be easily polymerized using a peroxide. Further, this compound

has a five-membered ring and is a stable material. In the case of a six-membered ring, ring-opening is liable to occur at the time of polymerization, and therefore, a resulting polymer becomes a mixture. In this case, physical properties such as heat resistance are liable to deteriorate.

5 4. Method for producing fluorinated polymers

[0039] The above fluorinated compound undergoes radical polymerization in accordance with an ordinary method, thereby allowing production of a fluorinated polymer. A peroxide is preferably used as a radical catalyst, but in order that a fluorine atom of the fluorine compound may not be substituted with a hydrogen atom, a perfluoroperoxide is used.

10 Example 1

<Synthesis of perfluoro-4-methyl-2-methylene-1,3-dioxolane>

15 Preparation of 2-carbomethyl-2-trifluoromethyl-4-methyl-1,3-dioxolane:

[0040] A 3L 3-necked flask equipped with a water-cooled condenser, a thermometer, a magnetic stirrer and a pressure-equalizing dropping funnel were made usable. The flask was charged with 139.4 g (1.4 mol) of a mixture of 2-chloro-1-propanol and 1-chloro-2-propanol. The flask was cooled to 0 °C and methyl trifluoropyruvate was slowly added thereto. After addition, the reaction mixture was stirred for additional 2 hours. Then 100 ml of DMSO and 194 g of potassium carbonate were further added during one hour. Stirring was continued for another 8 hours, thereby obtaining a reaction mixture. The reaction mixture obtained was poured into 1 L of water. Dichloromethylene extracts were combined with the organic phase. Subsequently, the reaction mixture was dried with magnesium sulfate. After removing the solvent, 245.5 g of crude product was obtained. The crude product was fractionally distilled at reduced pressure (12 Torr), and 230.9 g of pure product of 2-carbomethyl-2-trifluoromethyl-4-methyl-1,3-dioxolane was obtained. The boiling point of the pure product was 77 to 78°C, and the yield was 77%.

[0041] ¹HNMR (ppm): 4.2 to 4.6, 3.8 to 3.6 (CHCH₂, multiplet, 3H), 3.85 to 3.88 (COOCH₃, multiplet, 3H), 1.36 to 1.43 (CCH₃, multiplet, 3H);

[0042] ¹⁹FNMR (ppm): -81.3 (CF₃, s, 3F).

30 Fluorination of 2-carbomethyl-2-trifluoromethyl-4-methyl-1,3-dioxolane:

[0043] A 10L stirring-reactor vessel was loaded with 4 liters of 1,1,2-trichlorotrifluoroethane. The nitrogen flow was set at 1340 cc/min and the fluorine flow was set at 580 cc/min, thereby making the interior of the stirring-reactor vessel under a nitrogen/fluorine atmosphere. After 5 minutes, 290 g of the prepared 2-carbomethyl-2-trifluoromethyl-4-methyl-1,3-dioxolane was dissolved to 750 ml of 1,1,2-trichloro-trifluoroethane solution, and then this solution was added into the reactor at a rate of 0.5 ml/min. The reactor vessel was cooled to 0 °C. After all the dioxolane was added over 24 hours, the fluorine flow was stopped. After purging with nitrogen gas, an aqueous KOH solution was added to the reactor until it turned to slight alkali.

[0044] After removing volatile materials under reduced pressure. The residue was further dried under reduced pressure at 70°C for 48 hours, thereby obtaining a solid reaction product. The solid reaction product was dissolved in 500 ml of water and excess of hydrochloric acid was added to obtain two phases, that is, an organic phase and a water phase. The organic layer was separated and distilled under reduced pressure. As a result, perfluoro-2,4-dimethyl-1,3-dioxolane-2-carboxylic acid was produced. The boiling point of the main distillate was 103 to 106 °C /100 mmHg. The overall fluorination yield was 85 %.

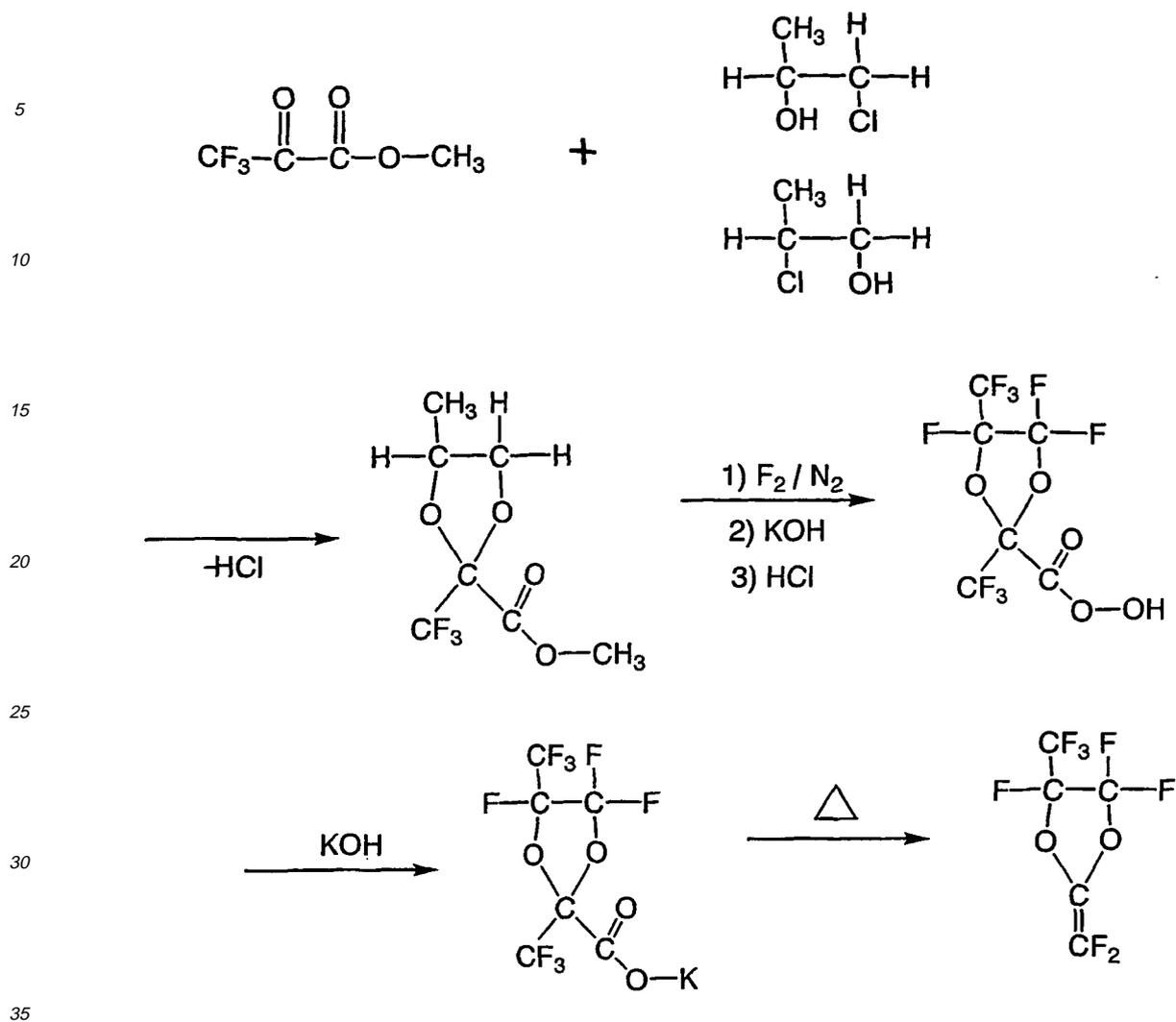
Synthesis of perfluoro-4-methyl-2-methylene-1,3- dioxolane:

[0045] Perfluoro-2,4-dimethyl-2-potassium carboxylate-1,3-dioxolane was obtained by neutralization of the above distillate with an aqueous KOH solution. The potassium salt was dried at 70 °C under vacuum for one day. The salt was decomposed with a stream of nitrogen or argon atmosphere at 250 to 280 °C to yield the product which was collected in a trap cooled to -78 °C, thereby obtaining perfluoro-4-methyl-2-methylene-1,3-dioxolane (yield: 82 %). The product had the boiling point of 45°C / 760 mmHg, and was identified using ¹⁹FNMR and GC-MS as below.

[0046] ¹⁹FNMR: -84 ppm (3F, CF₃), -129 ppm (2F, =CF₂);

[0047] GC-MS: m/e244 (Molecular ion) 225, 197, 169, 150, 131, 100, 75, 50.

[0048] Synthetic schemes according to Example 1 are schematically shown below.



Example 2

40 <Polymerization of perfluoro-4-methyl-2-methylene-1,3-dioxolane>

45 **[0049]** 100 g of perfluoro-4-methyl-2-methylene-1,3-dioxolane and 1g of perfluorobenzoyl peroxide were charged in a glass tube, which was then degassed and refilled with argon in two vacuum freeze-thaw cycles. The tube was sealed and heated at 50 °C for several hours. The content became solid. Further the tube was kept to be heated at 70 °C over night and 100g of a transparent bar was obtained.

[0050] The transparent bar was dissolved in Fluorinert FC-75 (produced by 3M Corporation) and a thin film of polymer was obtained by casting the solution on a glass plate. The glass transition temperature of the polymer was 117°C. The polymer was completely amorphous. The transparent bar was purified by precipitation from the hexafluorobenzene solution by adding chloroform thereto. The glass transition temperature of the product was increased to 133°C.

50 **[0051]** The refractive indexes at various wavelengths were shown by the line of A in Fig. 1, and the material dispersion of the polymer was shown in Fig. 2. It can be seen from such refractive indexes that the obtained polymer is suitable for optical fibers, optical waveguides, and photo masks.

55

Example 3

<Synthesis of perfluoro-4,5-dimethyl-2-methylene-1,3-dioxolane>

5 Synthesis of 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxolane:

[0052] A reaction mixture: 2.0 mol of 2,3-butanediol, 2.0 mol of methyl pyruvate, 10 g of a cation exchange resin (H form), and 1 L of absolute benzene were refluxed until no more water came to be produced in a flask fitted with a Dean-Stark trap, thereby obtaining 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxolane. The yield was 75% and the boiling point of the product was 45 °C/ 1.0 mmHg.

[0053] ¹HNMR: 1.3 ppm (6H, -CH₃), 1.56 ppm (3H, -CH₃), 3.77 ppm (3H, OCH₃), 3.5 to 4.4 ppm (m, 2H, -OCH-).

Synthesis of perfluoro-2,4,5-trimethyl-2-carboxylic acid-1,3-dioxolane:

15 **[0054]** 500 g of the obtained 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxolane was fluorinated with fluorine gas diluted with nitrogen in Fluorinert FC-75 (trade name) as described in Example 1. After completion of the reaction, nitrogen gas was purged for 30 minutes. The obtained mixture was then treated with an aqueous KOH solution to form an organic phase and a slightly-alkaline water phase. The water of the water phase was removed under reduced pressure, and a solid material was thereby obtained. The solid material obtained was acidified with concentrated hydrochloric acid and
20 distilled out, thereby obtaining perfluoro-2,4,5-trimethyl-2-carboxylic acid-1,3-dioxolane. The yield was 85 %, and the boiling point was 61 °C/2.5 mmHg.

Synthesis of perfluoro-4,5-dimethyl-2-methylene- 1,3-dioxolane:

25 **[0055]** Perfluoro-2,4,5-trimethyl-2-potassium carboxylate-1,3-dioxolane was obtained by neutralization of the above distillate with an aqueous KOH solution. The obtained potassium salt was dried at 70 °C under vacuum for one day. The salt was further decomposed with stream of nitrogen or argon at 250 to 280 °C to yield the product which was collected in a trap cooled to -78°C. As a result, perfluoro-4,5-dimethyl-2-methylene-1,3-dioxolane was obtained (yield: 78%). The boiling point of the product was 60°C. The product was identified using ¹⁹FNMR and GC-MS.

30 **[0056]** ¹⁹FNMR: -80 ppm (6F, -CF₃), -129 ppm (2F, =CF₂);

[0057] GC-MS: m/e294 (Molecular ion).

[0058] Synthetic schemes according to Example 2 are schematically shown below.

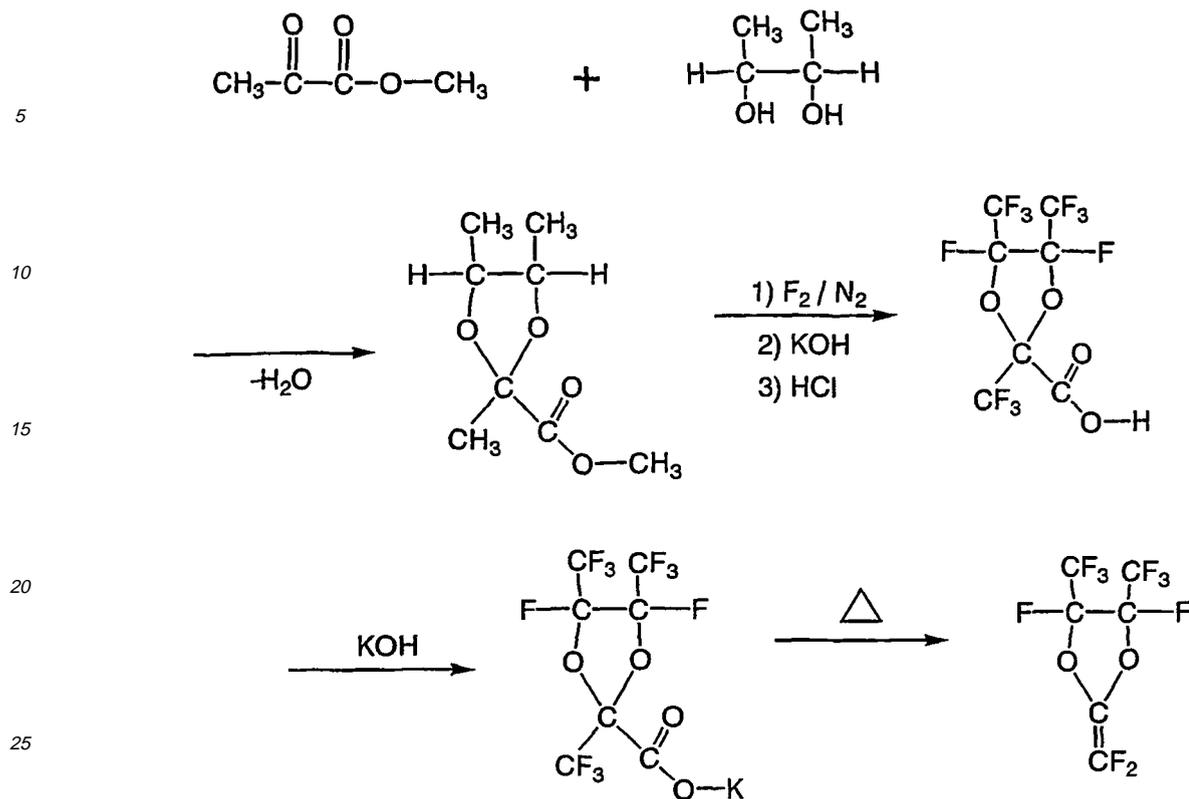
35

40

45

50

55



Example 4

<Polymerization of perfluoro-4,5-dimethyl-2-methylene-1,3-dioxolane>

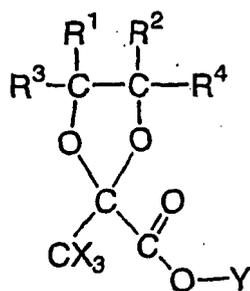
35 **[0059]** 10 g of the perfluoro-4,5-dimethyl-2-methylene-1,3-dioxolane obtained by Example 3 and 80 mg of perfluorobenzoylperoxide were charged in a glass tube, which was then degassed and refilled with argon in three vacuum freeze-thaw cycles. The tube was sealed and heated at 50 °C for one day. The content became solid and the tube was kept to be heated at 70 °C for 4 days. 10g of a transparent bar was obtained.

40 **[0060]** The transparent bar was purified by dissolving a part thereof in a hexafluorobenzene solution and also by precipitation from a hexafluorobenzene solution with chloroform being added thereto. The yield was 98% or greater. Solution polymerization of the monomer was performed in Fluorinert FC-75 (trade name) using perfluorobenzoyl peroxide as an initiator.

45 **[0061]** ^{19}F NMR of the obtained polymer was -80 ppm (6F, -CF₃), -100 to -120 ppm (2F, main chain) and -124 ppm (2F, -OCF). The refractive indexes of the obtained polymer are shown by the line B in Fig. 1, and the optical transmission thereof in the range of 200 to 2000 nm is shown in Fig. 3. It can be seen from such refractive indexes and optical transmission that the obtained polymer is suitable for optical fibers, optical wave guides, and photo masks.

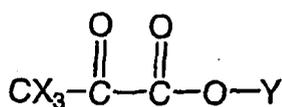
Claims

- 50 1. A method for producing a fluorinated compound represented by the following formula (3), the method comprising a step of obtaining the compound of the following formula (5)

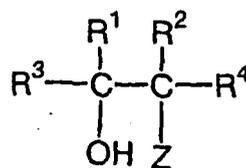


Formula (5)

wherein, in formula (5), X represents a hydrogen atom or a fluorine atom, Y represents a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, by fluorinating, in a fluorine-based solution under a fluorine gas atmosphere, a compound obtained by reacting at least one of kind of compound represented by the following formula (1) and at least one kind of compound represented by the following formula (2):

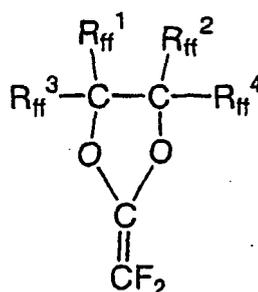


Formula (1)



Formula (2)

wherein in formula (1), X represents a hydrogen atom or a fluorine atom, and Y represents an alkyl group having 1 to 7 carbon atoms or a polyfluoroalkyl group having 1 to 7 carbon atoms; and in formula (2), Z represents a hydroxyl group, a chlorine atom, or a bromine atom, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and a step converting the compound of formula (5) into a compound of formula (3):

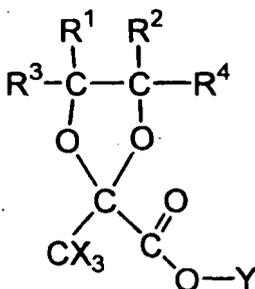


Formula (3)

wherein, in formula (3), R_{ff}¹ to R_{ff}⁴ each independently represent a fluorine atom or a perfluoroalkyl group having 1 to 7 carbon atoms.

- The method for producing a fluorinated compounds according to claim 1, wherein the fluorine gas atmosphere is a mixed atmosphere of nitrogen gas and fluorine gas, and a proportion of the nitrogen gas with respect to the fluorine gas is in a range from 2 to 4.

3. The method for producing a fluorinated compounds according to claim 1, wherein, in the step of fluorinating, a reaction temperature is kept in a range of 0 to 5°C, and stirring is carried out.
4. A compound represented by the following formula (5):

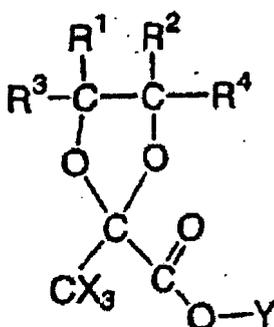


Formula (5)

wherein, in formula (5), X represents a hydrogen atom or a fluorine atom, Y represents a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and R¹ to R⁴ each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms.

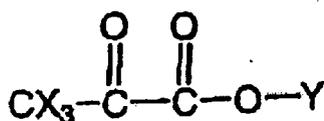
Patentansprüche

1. Verfahren zur Herstellung einer fluorierten Verbindung der nachfolgenden Formel (3), das folgende Schritte umfasst: die Gewinnung der Verbindung der nachfolgenden Formel (5):

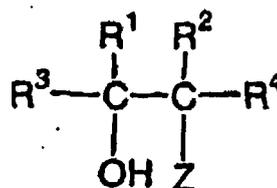


Formel (5)

worin X ein Wasserstoffatom oder ein Fluoratom darstellt, Y ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellt und R¹ bis R⁴ jeweils unabhängig ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellen, durch Fluorierung einer Verbindung in einer Lösung auf Fluorbasis unter einer Fluorgasatmosphäre, die durch Umsetzen mindestens einer Verbindung der nachfolgenden Formel (1) und mindestens einer Verbindung der nachfolgenden Formel (2) gewonnen wird:

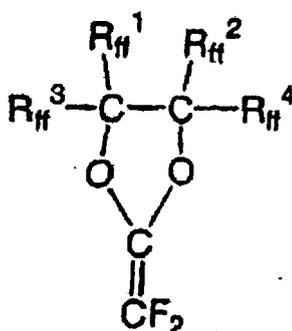


Formel (1)



Formel (2)

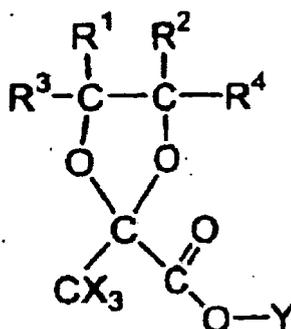
worin in Formel (1) X ein Wasserstoffatom oder ein Fluoratom darstellt und Y eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellt; und in Formel (2) Z eine Hydroxylgruppe, ein Chloratom oder ein Bromatom darstellt und R¹ bis R⁴ jeweils unabhängig ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellen, und die Umwandlung der Verbindung der Formel (2) in eine Verbindung der Formel (3):



Formel (3)

worin R_{ff}¹ bis R_{ff}⁴ jeweils unabhängig ein Fluoratom oder eine Perfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellen.

2. Verfahren zur Herstellung einer fluorierten Verbindung nach Anspruch 1, bei dem die Fluorgasatmosphäre eine gemischte Atmosphäre aus Stickstoffgas und Fluorgas ist und das Verhältnis von Stickstoffgas zu Fluorgas im Bereich von 2 bis 4 liegt.
3. Verfahren zur Herstellung einer fluorierten Verbindung nach Anspruch 1, bei dem die Reaktionstemperatur in dem Fluorierungsschritt unter Rühren in einem Bereich von 0 bis 5 °C gehalten wird.
4. Verbindung der nachfolgenden Formel (5):

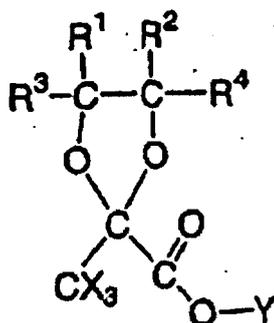


Formel (5)

worin X ein Wasserstoffatom oder ein Fluoratom darstellt, Y ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellt und R¹ bis R⁴ jeweils unabhängig ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 7 Kohlenstoffatomen oder eine Polyfluoralkylgruppe mit 1 bis 7 Kohlenstoffatomen darstellen.

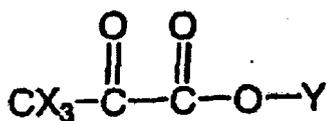
Revendications

1. Procédé de production d'un composé fluoré représenté par la formule (3) suivante, le procédé comprenant une étape d'obtention du composé de formule (5) suivante :

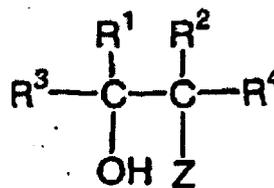


Formule (5)

dans laquelle, dans la formule (5), X représente un atome d'hydrogène ou un atome de fluor, Y représente un atome d'hydrogène, un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone, et R¹ à R⁴ représentent chacun indépendamment un atome d'hydrogène, un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone, par fluoration, dans une solution à base de fluor sous une atmosphère de fluor gazeux, d'un composé obtenu par la réaction d'au moins un type de composé représenté par la formule (1) suivante et d'au moins un type de composé représenté par la formule (2) suivante :

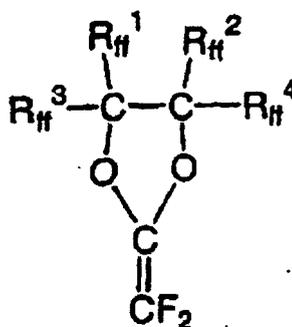


Formule (1)



Formule (2)

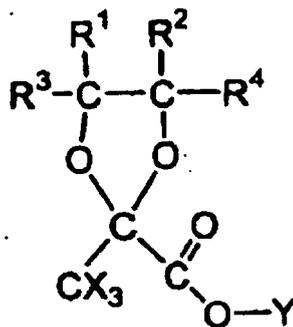
dans lesquelles, dans la formule (1), X représente un atome d'hydrogène ou un atome de fluor, et Y représente un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone ; et dans la formule (2), Z représente un groupe hydroxyle, un atome de chlore ou un atome de brome, et R¹ à R⁴ représentent chacun indépendamment un atome d'hydrogène, un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone, et une étape de conversion du composé de formule (5) en composé de formule (3) :



Formule (3)

dans laquelle, dans la formule (3), R_{ff}¹ à R_{ff}⁴ représentent chacun indépendamment un atome de fluor ou un groupe perfluoroalkyle contenant 1 à 7 atomes de carbone.

2. Procédé de production d'un composé fluoré selon la revendication 1, dans lequel l'atmosphère de fluor gazeux est une atmosphère mixte d'azote gazeux et de fluor gazeux, et la proportion de l'azote gazeux par rapport au fluor gazeux se situe dans une plage allant de 2 à 4.
3. Procédé de production d'un composé fluoré selon la revendication 1, dans lequel, dans l'étape de fluoration, la température réactionnelle est maintenue dans la plage allant de 0 °C à 5 °C, et une agitation est mise en oeuvre.
4. Composé représenté par la formule (5) suivante :



Formule (5)

dans laquelle, dans la formule (5), X représente un atome d'hydrogène ou un atome de fluor, Y représente un atome d'hydrogène, un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone, et R¹ à R⁴ représentent chacun indépendamment un atome d'hydrogène, un groupe alkyle contenant 1 à 7 atomes de carbone ou un groupe polyfluoroalkyle contenant 1 à 7 atomes de carbone.

FIG.1

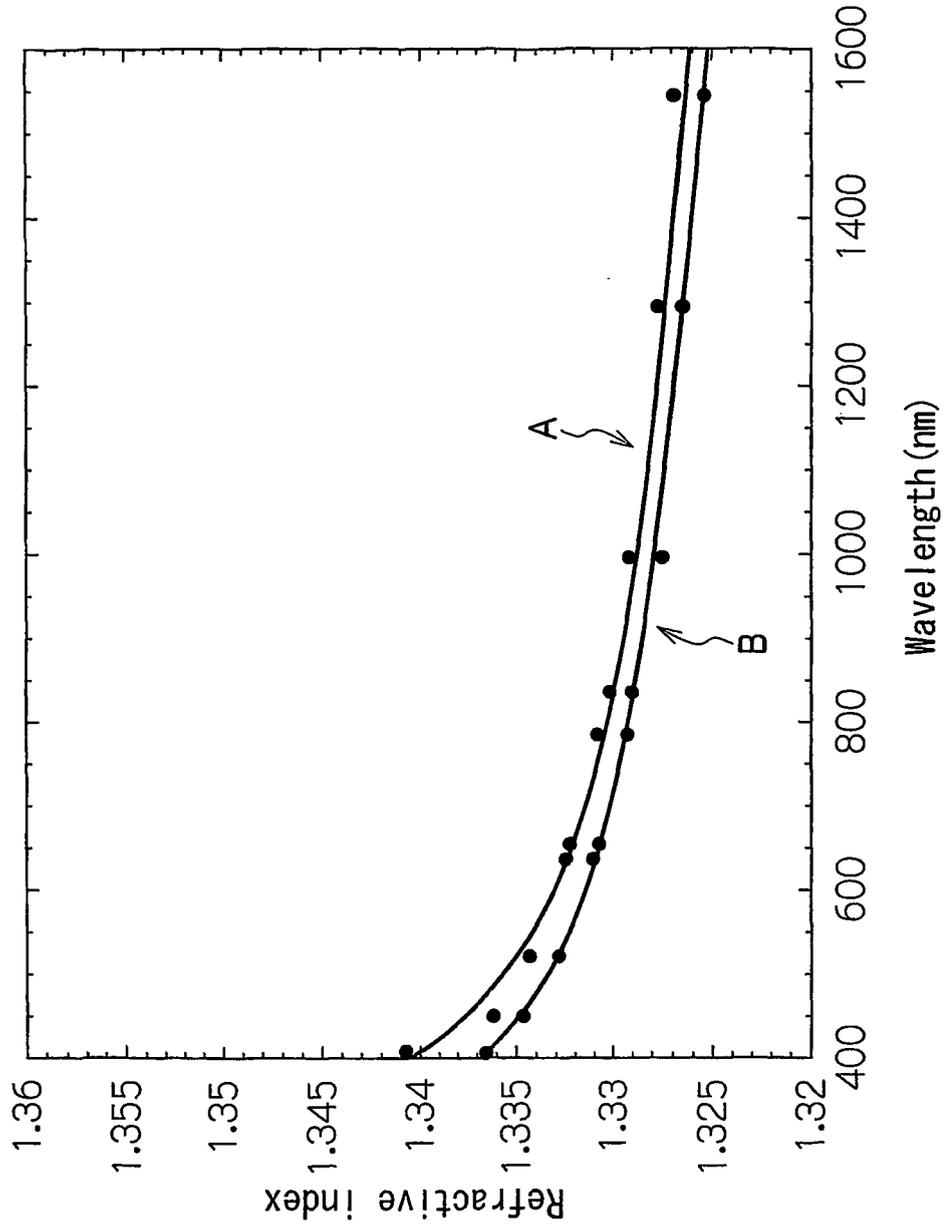


FIG.2

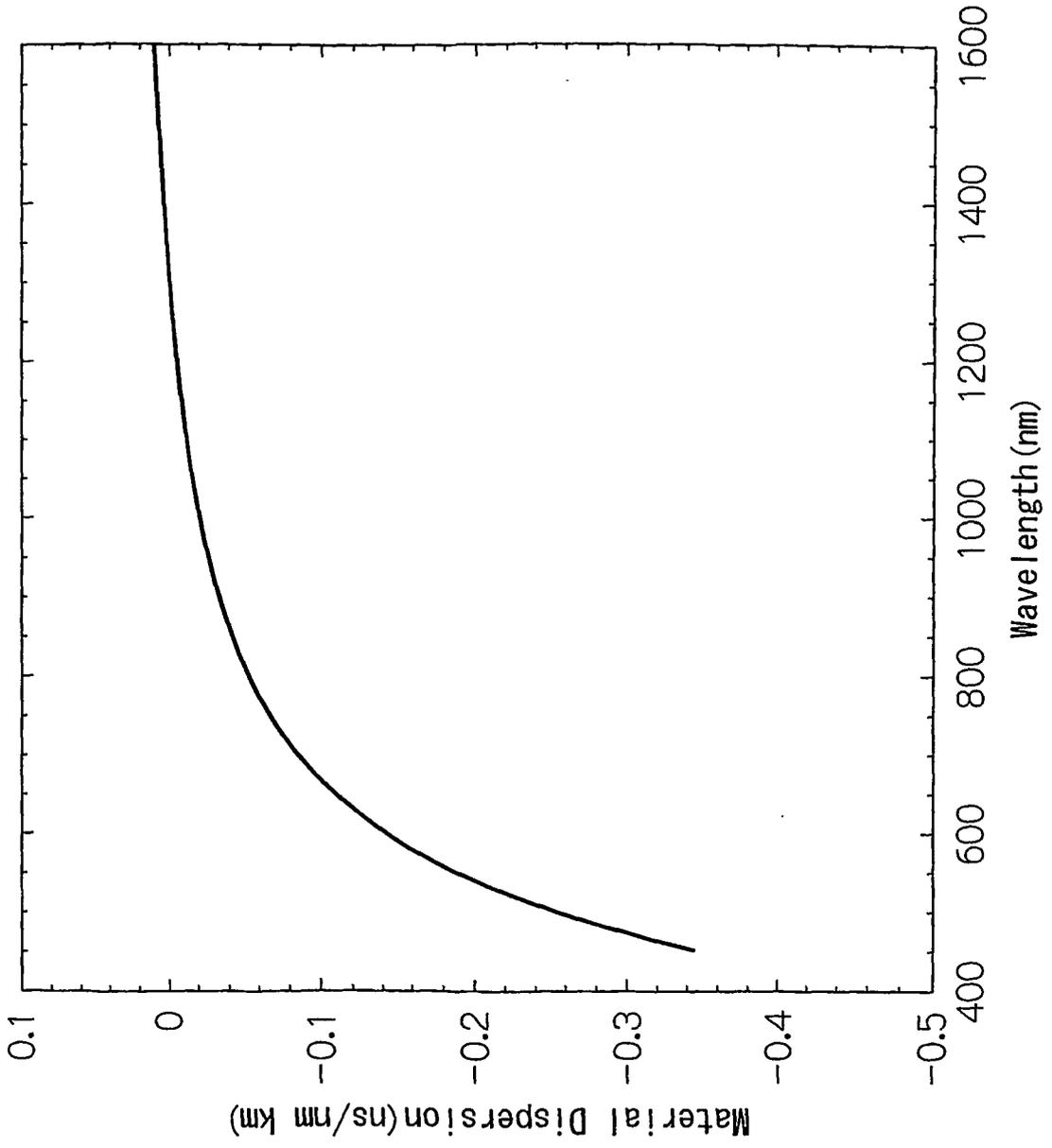
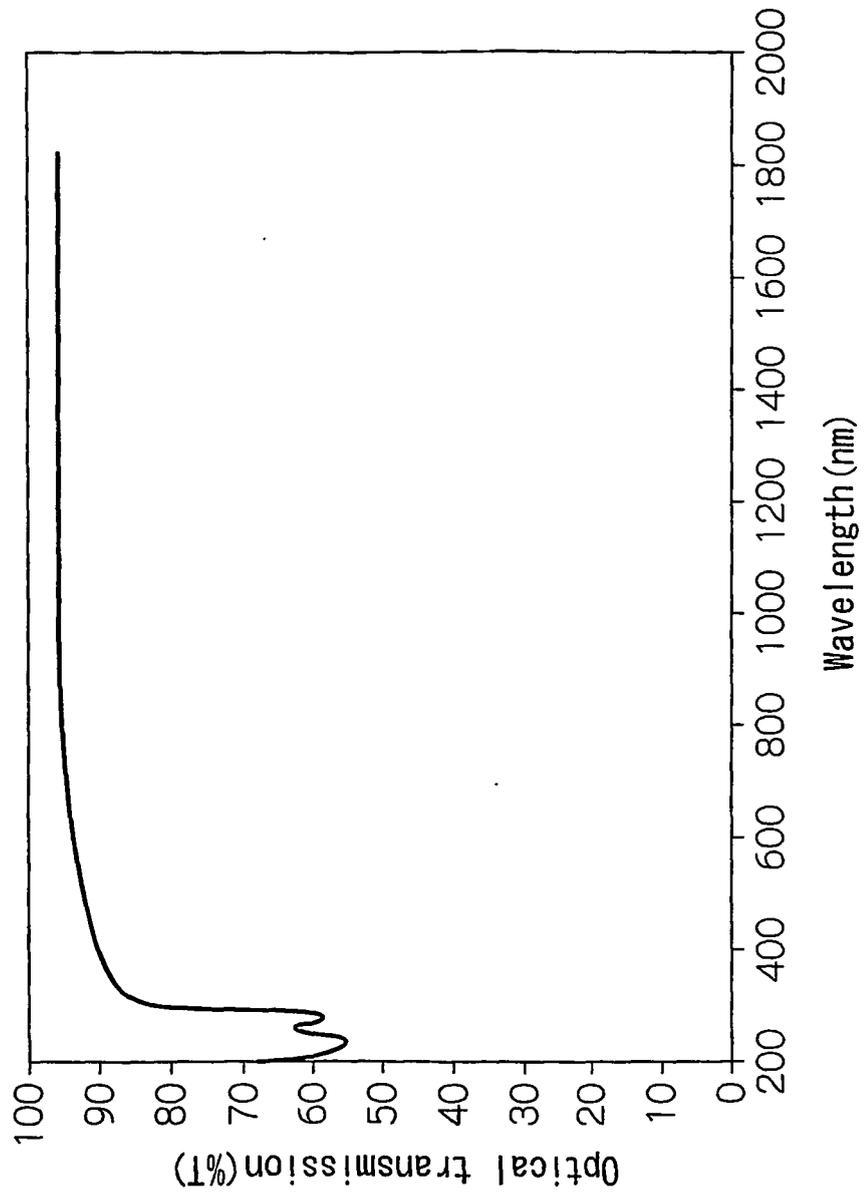


FIG.3



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3308107 A [0003]
- US 3450716 A [0003]
- US 3978030 A [0004]
- JP 5339255 A [0004]
- JP 5213929 A [0007]
- CA 464643 A2 [0008]

Non-patent literature cited in the description

- **V.S. Yuminov ; V.S. Yuminov et al.** *Izvestiya A Kademii Nank SSSR, Seriya Khimicheskaya*, February 1988, 392-395938 [0003]
- Synthetic Fluorine Chemistry. J.Wiley and Sons. Inc, 1992 [0027]
- **R.J.Lagow ; T.R.Bierschenk ; T.J.Juhlke ; H.kawa.** Polyether Synthetic Method [0027]