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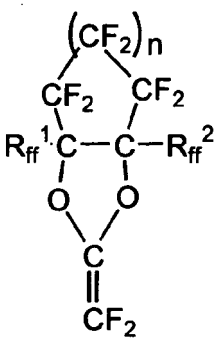
Remarks:
This application was filed on 22-05-2009 as a divisional application to the application mentioned under INID code 62.

(54) **Fluorinated compounds, fluorinated polymers of the fluorinated compounds, and optical or electrical materials using the polymers**

(57) A fluorinated compound represented by the following formula (4):



Formula (4)

wherein, in formula (4), R_{ff}^1 and R_{ff}^2 each independently represent a fluorine atom or a perfluoroalkyl group having 1 to 7 carbon atoms, and n represents an integer from 1 to 4.

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Description

BACKGROUND OF THE INVENTION

Technical Field

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

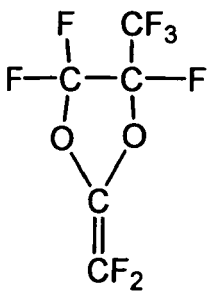
Related Art

[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.

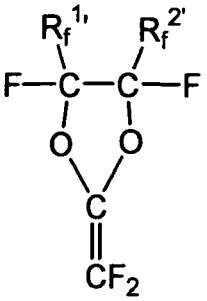
[0003] A fluorinated polymer is obtained by polymerization of a fluorinated compound having a polymeric unsaturated group. As an example of fluorinated polymers, 1,3-dioxolane derivatives and the like are disclosed in U.S. Patent No. 3,308,107, U.S. Patent No. 3,450,716; Izvestiya A Kademii Nank SSSR, 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.

[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 or in U.S. Patent No. 3,308,107, 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.

Formula (A)



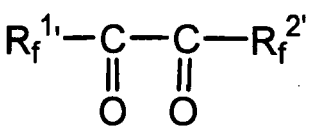
Formula (B)



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

[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.

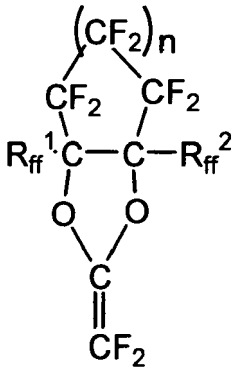
Formula (C)



SUMMARY OF THE INVENTION

[0007] 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.

[0008] A first aspect of the present invention is a fluorinated compound represented by the following formula (4):



Formula (4)

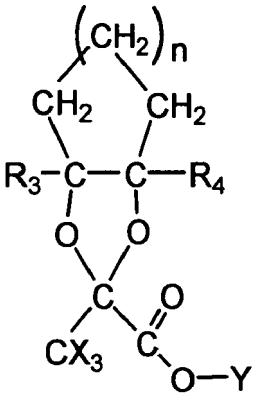
wherein, in formula (4), R_{ff}^1 and R_{ff}^2 each independently represent a fluorine atom or a perfluoroalkyl group having 1 to 7 carbon atoms, and n represents an integer from 1 to 4.

[0009] A second aspect of the present invention is a fluorinated polymer obtained by polymerization of the fluorinated compound according to the first aspect.

[0010] A third aspect of the present invention is an optical or electrical material comprising the fluorinated polymer according to the second aspect.

[0011] A fourth aspect of the present invention is an optical or electrical material according to the third aspect, wherein the optical material is an optical wave guide, an optical lens, a prisms, a photo mask, or an optical fiber.

[0012] A fifth aspect of the present invention is a compound represented by the following formula (6):



Formula (6)

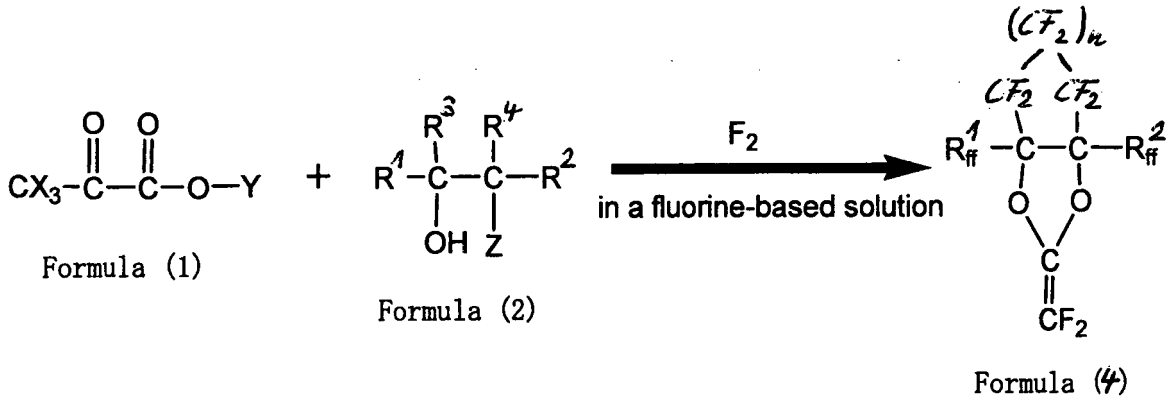
wherein, in formula (6), X represents a hydrogen atom or a fluorine atom, Y represents a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, R^3 or R^4 each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, and n represents an integer from 1 to 4.

DETAILED DESCRIPTION OF THE INVENTION

1. Method for producing fluorinated compounds

[0013] A description will be given of a method for producing fluorinated compounds, that are 1,3-dioxolane derivatives, according to the present invention.

[0014] 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) (2) in a fluorine-based solution in a flow of fluorine gas.



Formula (1)

Formula (2)

Formula (4)

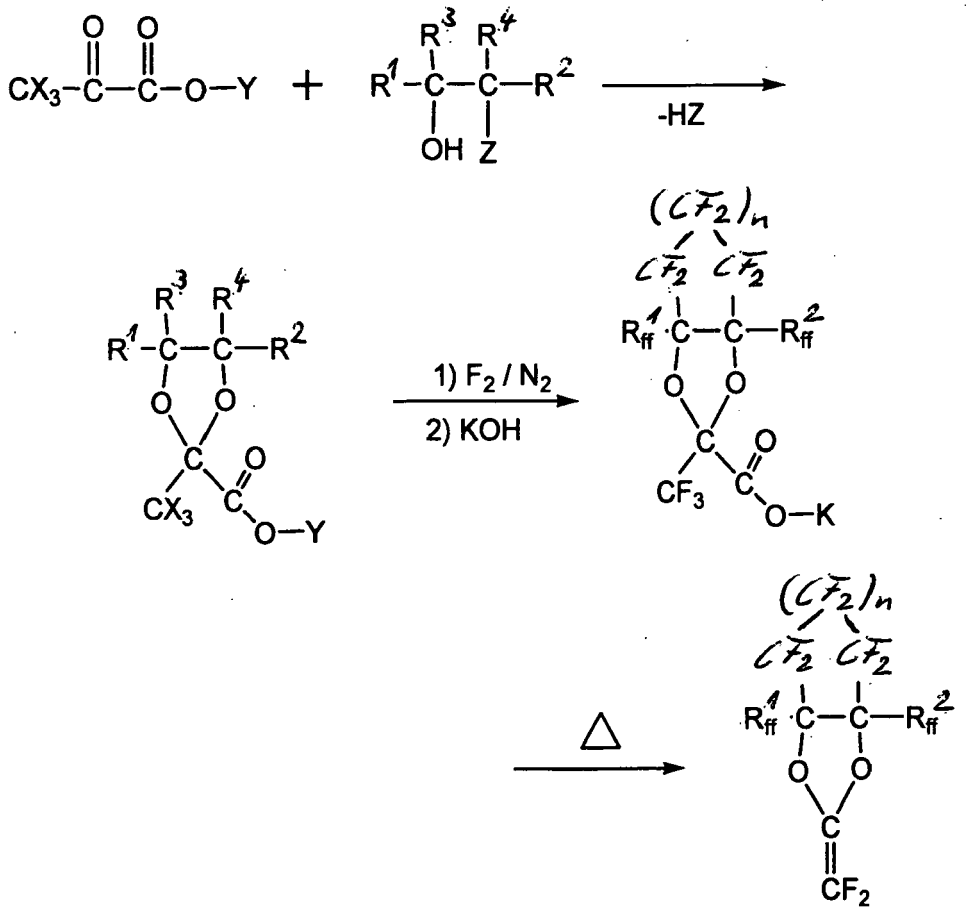
[0015] In Formula (1), X represents a hydrogen atom or a fluorine atom. From the viewpoint of ready availability, X is preferably a hydrogen atom. Y represents an alkyl group having 1 to 7 carbon atoms, preferably 1 to 3 carbon atoms, or a polyfluoroalkyl group having 1 to 7 carbon atoms, preferably 1 to 3 carbon atoms, more preferably a perfluoroalkyl group having 1 to 3 carbon atoms. Specially preferably, Y represents an alkyl group having 1 to 3 carbon atoms

[0016] In Formula (2), Z represents a hydroxyl group, chlorine atom, or bromine atom.

[0017] In Formula (2), R^1 and R^2 each independently represent a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, or an 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 R^1 and R^2 may be hydrogen atom, alkyl group, or polyfluoroalkyl group. More preferably, R^1 and R^2 each independently represent a hydrogen atom, or an alkyl group having 1 to 7 carbon atom because of cost-effective. Specifically preferably, R^1 and R^2 each independently represent a hydrogen atom, or an alkyl group having 1 to 3 carbon atom. R^3 and R^4 are bonded to each other to form a ring and are alkyl groups, having together from 3 to 6 carbon atoms.

[0018] In Formula (4), R_{ff}^1 and R_{ff}^2 each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 7 carbon atoms. Preferably, R_{ff}^1 and R_{ff}^2 each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 3 carbon atoms.

[0019] Reaction schemes of these compounds are exemplified below, but the present invention is not limited to the same.



[0020] The production process of the present invention is broadly divided into, preferably, at least four steps as below.

(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.

[0021] These four steps (1) to (4) will be described below in detail.

Step (1):

[0022] 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.

[0023] 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):

[0024] 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, Chaper 5: Polyether Synthetic

Method.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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):

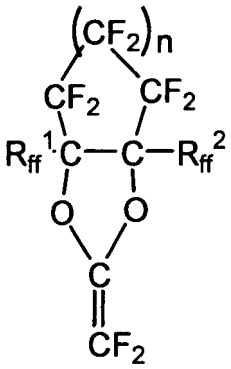
[0029] A carboxylate salt is produced from the fluorine compound obtained by step (2) by a base. As the base, potassium hydroxide, sodium hydroxide, cesium hydroxide, and the like are preferable. Potassium hydroxide is more preferable.

Step (4):

[0030] 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.

[0031] In the production method of the present invention, other steps in addition to the above steps (1) to (4) can be added.

[0032] A compound represented by the following formulae (4) is a novel compound.



Formula (4)

[0033] R_{ff}^1 and P_{ff}^2 each independently represent a fluorine atom, or a perfluoroalkyl group having 1 to 7 carbon atoms, and n represents an integer of 1 to 4, preferably, an integer of 1 to 2.

4. Method for producing fluorinated polymers

[0034] 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.

5. Application of Fluorinated polymer

[0035] A polymer obtained by polymerization of the compound represented by Formula (4) can be suitably used for optical or electrical materials. This polymer has a high glass transition temperature and it is amorphous material. Therefore, such polymer can be suitably used for plastic optical fibers, light wave guides, optical lenses, prisms, photo masks, and the like, more suitably used for plastic optical fibers, light wave guides material, optical lenses.

Example 1

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

Synthesis of 2-methyl-2-methoxycarboxyl-4,5-cyclotetramethylene-1,3-dioxolane:

[0036] A reaction mixture: 100 g (1 mol) of 1,2-cyclohexanediol, 204 g (2 mols) of methyl pyruvate, 1,5 L of absolute benzene, and 10 g of a cation exchange resin (H form) was refluxed until no more water came to be produced in a flask fitted with a Dean-Stark trap. The cation exchange resin was removed by filtration. The product was distilled at 65 °C/5 mmHg, thereby obtaining 2-methyl-2-methoxycarboxyl-4,5-cyclotetramethylene-1,3-dioxolane. The yield was 50 to 60 %.

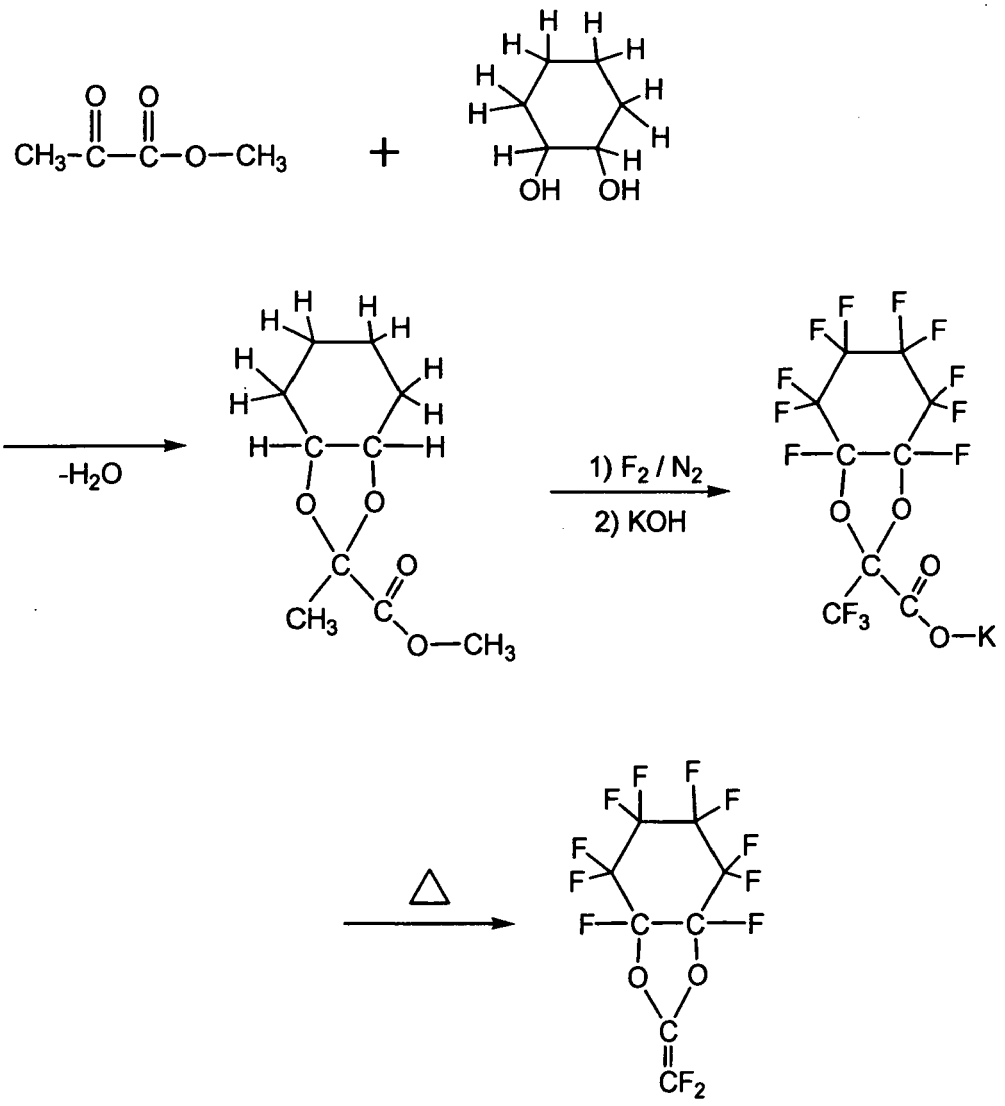
Fluorination of 2-methyl-2-methoxycarboxyl-4,5-cyclotetramethylene-1.3-dioxolane:

[0037] The obtained 2-methyl-2-methoxycarboxyl-4,5-cyclotetramethylene-1,3-dioxolane was fluorinated in a fluorinated solvent, Fluorinert FC-75 (trade name) with F_2/N_2 as described here in below. 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 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 completion of the reaction, by removing the solvent and produced hydrogen fluoride, and then treating the fluorinated product with an aqueous KOH solution, perfluoro-2-methyl-2-potassium carboxylate-4,5-cyclotetramethylene-1,3-dioxolane was obtained. The obtained potassium salt was dried by heating at 60 °C under reduced pressure (yield: 75 %) and the dried potassium salt was decomposed at 250 °C in the nitrogen gas atmosphere. The product; perfluoro-4,5-cyclotetramethylene-2-methylene-1,3-dioxolane was collected in a trap cooled to -78 °C and the yield thereof was 85 %. The boiling point of the product was 60 °C. The product was identified using ^{19}FNMR and GC-MS.

[0038] ^{19}FNMR: -137 ppm (2F, $=CF_2$), 126 to 134 ppm (8F, CF_2), -125 ppm (2F, OCF);

[0039] GC-MS: m/e360 (Molecular ion).

[0040] Synthetic schemes according to Example 1 are schematically shown below.



Example 2

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

[0041] 10 g of the perfluoro-4,5-cyclotetramethylene-2-methylene-1,3-dioxolane obtained by Example 1 and 80 mg 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 12 hours. The content of tube became solid and the tube was kept to be heated at 70 °C over night. 10g of a transparent rod was obtained.

[0042] The resulting polymer was completely amorphous and transparent. The refractive indexes of the polymer were 1.3160 (632.8 nm) and 1.3100 (1544 nm), and the glass transition temperature thereof was about 160 °C.

[0043] ^{19}FNMR: $^{-}$120 to $^{-}$140 ppm (8F, CF_2), $^{-}$100 to $^{-}$118 ppm (2F, main chain), and 120 ppm (2F, $^{-}$OCF). It can be seen from the viewpoint of a high glass transition temperature that the obtained polymer is less subject to heat deformation, and is suitable for electrical materials, *optical fibers, optical wave guides*, and the like.

Example 3

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

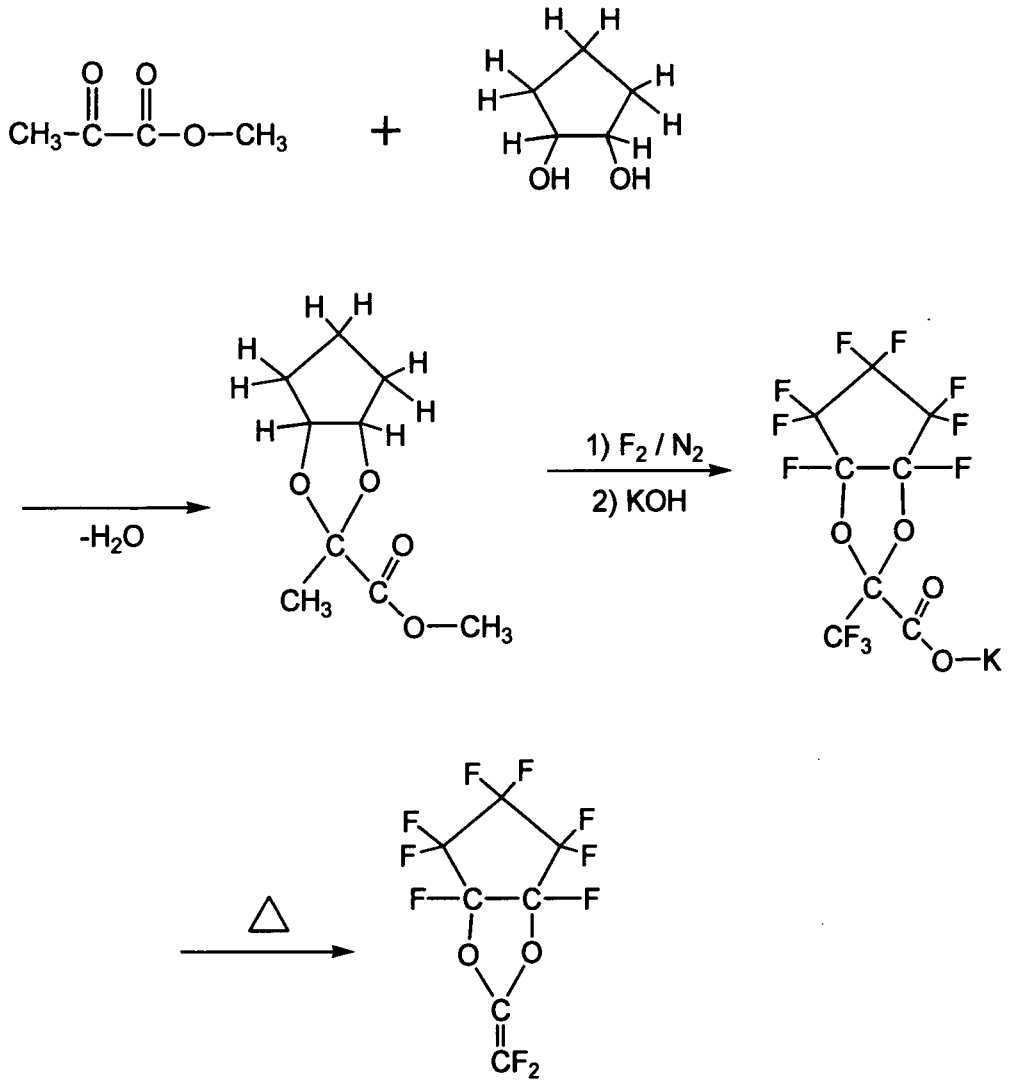
Synthesis of 2-methyl-2-methoxycarboxyl-4,5-cyclotrimethylene-1,3-dioxolane:

[0044] A reaction mixture: 102 g (1 mol) of 1,2-cyclopentanediol, 204 g (2 mols) of methyl pyruvate, 1.5 L of absolute benzene, and 10 g of a cation exchange resin (H form) was refluxed until no more than water came to be produced. After the cation exchange resin was removed by filtration, the product was distilled at 67 °C/20 mmHg, thereby obtaining 2-methyl-2-methoxycarboxyl-4,5-cyclotrimethylene-1,3-dioxolane. The yield was 60 to 70 %. 55

Fluorination of 2-methyl-2-methoxycarboxyl-4,5-cyclotrimethylene-1,3-dioxolane:

[0045] The obtained 2-methyl-2-methoxycarboxyl-4,5-cyclotrimethylene-1,3-dioxolane was fluorinated in a fluorinated solvent, Fluorinert FC-75 (trade name) with F_2/N_2 as described herein below. 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 dioxolane was dissolved to 750 ml of 1,1,2-trichlorotrifluoroethane 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. The reaction product was treated with potassium hydroxide to thereby produce perfluoro-2-methyl-2-potassium carboxylate-4,5-cyclotrimethylene-1,3-dioxolane. The potassium salt obtained was dried by heating at 60 °C under reduced pressure. The yield was 82 %. The dried potassium salt was decomposed at 260 °C in the flow of argon gas. The crude product was distilled at 85 °C to produce perfluoro-4,5-cyclotrimethylene-2-methylene-1,3-dioxolane (yield: 79 %).

[0046] Synthetic schemes according to Example 3 are schematically shown below.



Example 4

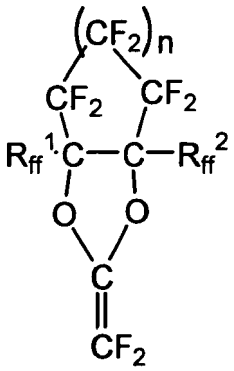
<Polymerization of perfluoro-4,5-cyclotrimethylene-2-methylene-1,3-dioxolane>

[0047] 20 g of the perfluoro-4,5-cyclotrimethylene-2-methylene-1,3-dioxolane obtained by Example 3 and 150 mg of perfluorobenzoyl peroxide were charged in a glass tube. The polymerization was carried out as described herein below. 100 g of the 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. A transparent amorphous polymer was obtained. The glass transition temperature of the polymer was found to be 150 °C.

[0048] As described above, the polymers obtained are highly transparent and amorphous and also have a high glass transition temperature, and therefore, they are found as excellent materials that can be used for various applications of optical fibers, electrical materials, and the like.

Claims

1. A fluorinated compound represented by the following formula (4):



Formula (4)

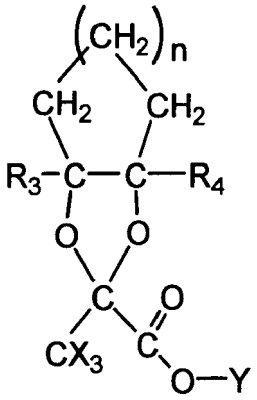
wherein, in formula (4), R_{ff}^1 and R_{ff}^2 each independently represent a fluorine atom or a perfluoroalkyl group having 1 to 7 carbon atoms, and n represents an integer from 1 to 4.

2. A fluorinated polymer obtained by polymerization of the fluorinated compound according to claim 1.

3. An optical or electrical material comprising the fluorinated polymer according to claim 2.

4. An optical or electrical material according to claim 3, wherein the optical material is optical wave guides, an optical lens, a prisms, a photo masks, or an optical fiber.

5. A compound represented by the following formula (6):



Formula (6)

wherein, in formula (6),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, R^3 or R^4 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 n represents an integer from 1 to 4.

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EUROPEAN SEARCH REPORT

Application Number
EP 09 00 6883

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 3 308 107 A (SELMAN STANLEY ET AL) 7 March 1967 (1967-03-07) * the whole document * -----	1-5	INV. C07D317/06 C07D317/16
P,X	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 * the whole document * -----	1-5	
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D,A	JP 05 339255 A (ASAHI GLASS CO LTD) 21 December 1993 (1993-12-21) * the whole document * -----	1-5	
			TECHNICAL FIELDS SEARCHED (IPC) C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	10 July 2009	Goss, Ilaria

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 09 00 6883

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10-07-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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