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(54) **HYDROPHILIC POROUS POLYTETRAFLUOROETHYLENE MEMBRANE**

HYDROPHILE PORÖSE POLYTETRAFLUORETHYLENMEMBRAN

MEMBRANE POREUSE DE POLYTÉTRAFLUOROÉTHYLÈNE HYDROPHILE

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- **ZHAOLIANG CUI ET AL: "Recent progress in fluoropolymers for membranes", PROGRESS IN POLYMER SCIENCE., vol. 39, no. 1, 1 January 2014 (2014-01-01), pages 164-198, XP055299292, GB ISSN: 0079-6700, DOI: 10.1016/j.progpolymsci.2013.07.008**

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## Description

## BACKGROUND OF THE INVENTION

5 [0001] The properties of porous PTFE membrane, including its mechanical strength, chemical resistance or inertness, non-adhesiveness, excellent dielectric property, thermal stability at high temperature and low coefficient of friction make it very attractive for various applications. However, for certain applications, it will be beneficial to improve its wetting characteristics without affecting its intrinsic properties. Efforts have been made to modify one or more properties of PTFE membranes. However, many of these efforts result in reduction in one or more of PTFE's attractive properties, for example, mechanical strength.

10 [0002] The foregoing shows that there exists an unmet need for preparing porous PTFE membranes with improved wetting characteristics without significantly affecting its mechanical strength.

[0003] Zhaoliang Cui et al. describe in the article "Recent progress in fluoropolymers for membranes", published in Progress in Polymer Science 39 (2014), pages 164-198, structures and properties of fluoropolymers for membranes, the preparation and modification methods of fluoropolymer membranes, and their application.

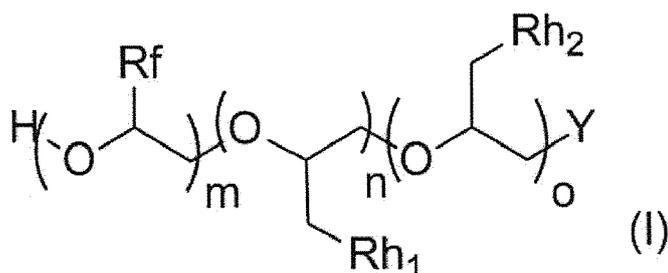
## BRIEF SUMMARY OF THE INVENTION

20 [0004] The present invention relates to a method of preparing a hydrophilic porous PTFE membrane as set out in claim 1. Furthermore the invention relates to a hydrophilic porous membrane obtainable by the method of the present invention as set out in claim 3. Finally the invention relates to a process of filtering a fluid as defined in claim 10.

[0005] The present invention provides a hydrophilic porous membrane obtainable by the claimed process and comprising polytetrafluoroethylene (PTFE) and an amphiphilic copolymer of formula (I):

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35 wherein the amphiphilic copolymer is a random or block copolymer, Rf is a perfluoro-substituted group, whereas Rh<sub>1</sub> and Rh<sub>2</sub> are hydrophilic groups as defined in the claims or chlorine, m and n are independently from 10 to 1000, and o is from 0 to 1000, and Y is hydroxyl.

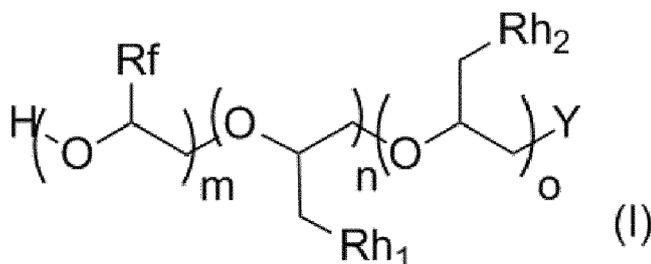
[0006] The invention further provides a method of preparing a hydrophilic porous PTFE membrane comprising:

- 40 (i) preparing a blend comprising PTFE and a amphiphilic copolymer, and optionally a lubricant;  
 (ii) extruding the blend into a tape;  
 (iii) biaxially stretching the tape to obtain a hydrophilic porous membrane;

45 wherein the amphiphilic copolymer is of formula (I):

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wherein the amphiphilic copolymer is a homopolymer or a random or block copolymer, Rf is a perfluoro-substituted group, whereas Rh<sub>1</sub> and Rh<sub>2</sub> are hydrophilic groups or chlorine, m, n and o are independently from 0 to 1000, provided m+n+o is greater than or equal to 10, and Y is hydroxyl.

[0007] The method may further comprise a step of annealing the hydrophilic porous membrane.

[0008] Also disclosed is that the hydrophilic porous membrane can optionally be reacted with an acid to modify the chemical structure of the amphiphilic polymer.

[0009] The hydrophilic porous membranes share many of the advantages of PTFE membranes, for example, mechanical strength, and at the same time, exhibit high levels of water wettability.

[0010] The invention further provides methods of filtering fluids through these hydrophilic porous PTFE membranes.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0011]

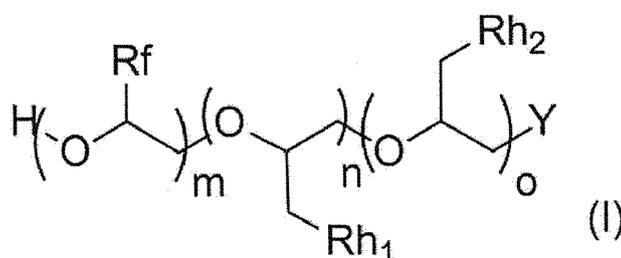
Figure 1 depicts an optical micrograph of the surface of a hydrophilic PTFE membrane annealed at 150 °C.

Figure 2 depicts an optical micrograph of the surface of a hydrophilic PTFE membrane annealed at 250 °C.

Figure 3 depicts an optical micrograph of the surface of a hydrophilic PTFE membrane annealed at 350 °C.

#### DETAILED DESCRIPTION OF THE INVENTION

[0012] In accordance with an embodiment, the invention provides a hydrophilic porous membrane obtainable by the claimed process and comprising polytetrafluoroethylene (PTFE) and an amphiphilic copolymer of formula (I):



wherein the amphiphilic copolymer is a random or block copolymer, Rf is a perfluoro-substituted group, whereas Rh<sub>1</sub> and Rh<sub>2</sub> are hydrophilic groups or chlorine, m and n are independently from 10 to 1000, o is from 0 to 1000, and Y is hydroxyl.

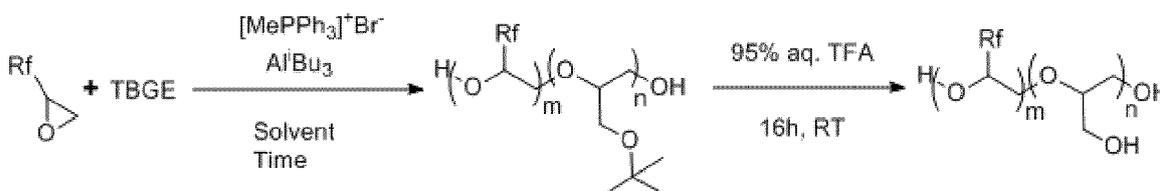
[0013] In embodiments, m, n and o represent the degrees of polymerization of the respective monomers, and are each independently from about 10 to about 1000 or more, preferably from about 100 to about 200.

[0014] In other embodiments, m, n and o represent the mole fraction of the monomers present in the copolymer and each can independently range between 0 to 99 mole %, preferably 10 to 40 mole %.

[0015] The respective monomer blocks can be present in the block copolymer in any suitable mass %, for example, in an embodiment, from about 99%: about 1% to about 50%: about 50%, preferably from about 90%: about 10% to about 70%: about 30%, and more preferably from about 75%: about 25%.

[0016] The copolymer can be of any suitable molecular weight, for example, in an embodiment, a number or weight (Mn or Mw) average molecular weight from about 10 kDa to about 1000 kDa, preferably from about 75 kDa to about 500 kDa, and more preferably from about 250 kDa to about 500 kDa.

[0017] The amphiphilic copolymers used can be prepared by any suitable method, for example, by ring opening polymerization of a fluorinated epoxy compound. See for example, US 2009/0030175 A1. The ring opening polymerization is conducted in the presence of a trialkyl aluminum and a salt having an organic counter cation, as illustrated below on a mixture of two monomers: perfluoroalkyl epoxide and t-butyl glycidyl ether (TBGE). The resulting diblock copolymer is reacted with an acid such as trifluoroacetic acid to remove the t-butyl group and provide a copolymer of perfluorinated ethylene oxide and hydroxymethyl ethylene oxide:



[0018] For example, to prepare a triblock copolymer, a diblock copolymer such as the diblock block copolymer obtained from the perfluorinated ethylene oxide and TGBE is first prepared, and a third monomer can be added and the polymerization continued.

[0019] The polymerization of the monomers is conducted in a suitable solvent, for example, a fluorinated solvent. The solvent can be selected based on the appropriate solubility of the fluorinated polymer to be formed. An example of a suitable solvent is hexafluorobenzene. Examples of suitable solvents include aromatic hydrocarbons such as benzene, toluene, and xylene, aliphatic hydrocarbons such as n-pentane, hexane, and heptane, alicyclic hydrocarbons such as cyclohexane, and halogenated hydrocarbons such as dichloromethane, dichloroethane, dichloroethylene, tetrachloroethane, chlorobenzene, dichlorobenzene, and trichlorobenzene, as well as mixtures thereof.

[0020] The monomer concentration can be in the range of 1 to 50 wt%, preferably 2 to 45 wt%, and more preferably 3 to 40 wt %.

[0021] The polymerization can be carried out at any suitable temperature, for example, from 0 to 150 °C, preferably 0 to 80 °C.

[0022] To prepare a block copolymer, for example, the polymerization can be carried out for any time suitable to obtain the appropriate chain length of each of the blocks, which can be from about 1 minute to 100 hours.

[0023] The amount of catalyst can be chosen in any suitable amount. For example, the molar ratio of the catalyst to a monomer can be about 1:10 to about 1:1000, preferably about 1:50 to 1:500, and more preferably about 1:100 to about 1:200. For example, the molar ratio of the catalyst to a monomer could be 1:n, 1:m, or 1:o, where n, m, and o are the average degrees of polymerization.

[0024] The polymers can be isolated by a suitable technique, for example, precipitation with a nonsolvent.

[0025] The copolymers can be characterized for their molecular weights and molecular weight distributions by any known techniques. For example, a MALS-GPC technique can be employed. The technique uses a mobile phase to elute, via a high pressure pump, a polymer solution through a bank of columns packed with a stationary phase. The stationary phase separates the polymer sample according to the chain size followed by detecting the polymer by three different detectors. A series of detectors can be employed, e.g., an Ultraviolet detector (UV-detector), followed by a multi-angle laser light scattering detector (MALS-detector), which in turn, is followed by a refractive index detector (RI-detector) in a row. The UV-detector measures the polymer light absorption at 254 nm wavelength; the MALS-detector measures the scattered light from polymer chains relative to mobile phase.

[0026] The polydispersity of the copolymers depends on the reaction conditions. For example, the copolymers have an Mw/Mn of 1.05 to 2.5, preferably 1.1 to 1.2.

[0027] Examples of amphiphilic copolymers, their structures, and representative formulations for forming hydrophilically modified PTFE membranes are set forth in Table 1.

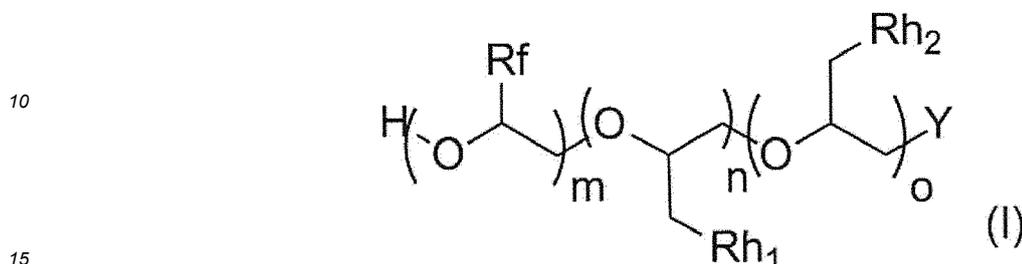
Table 1. Examples of amphiphilic copolymers and formulations

Batch MS-06-	Acronym	Structure	Formulation
9	pPF8PO-r-pTBGE		25wt% 25wt% of Acetone 50wt% of Isopar G
37	pPF6EtGE-r-pECH		25wt% 25wt% of Acetone 50wt% of Isopar G
38 - FIN	pPF8PO-r-Pg		25wt% 25wt% of Acetone 50wt% of Isopar G

[0028] The present invention further provides a method of preparing a hydrophilic porous PTFE membrane comprising:

- (i) preparing a blend comprising PTFE and an amphiphilic copolymer, and optionally a lubricant;  
 (ii) extruding the blend into a tape;  
 (iii) biaxially stretching the tape to obtain a hydrophilic porous membrane; optionally

5 wherein the amphiphilic copolymer is of formula (I):



wherein the amphiphilic copolymer is a random or block copolymer, Rf is a perfluoro-substituted group, whereas Rh<sub>1</sub> and Rh<sub>2</sub> are hydrophilic groups as claimed or chlorine, m and n are independently from 10 to 1000, o is from 0 to 1000, and Y is hydroxyl.

20 **[0029]** The method optionally comprises a step of annealing the hydrophilic porous membrane.

**[0030]** Also disclosed is that the hydrophilic porous membrane can be reacted with an acid to modify the chemical structure of the amphiphilic copolymer.

25 **[0031]** The required amount of a PTFE powder is mixed with a solution of the copolymer in a suitable solvent, for example, a ketone solvent such as acetone or methyl ethyl ketone to obtain a blend, which is then mixed with a lubricant such as odorless mineral spirits, e.g., Isopar G, and the resulting paste is subjected to shear, for example, in a twin roller, and formed into a billet under a pressure of about 300 psi or more, at least twice, each for a period of about 55 sec. The resulting billets are equilibrated at room temperature for about 12 hrs or more. The billets are then extruded into the desired shape. For example, extrusion is performed at 26 mm die gap size, maximum pressure and constant temperature of 55 °C resulting in a tube shaped PTFE tape. Next, the tube shaped tape is cut open along the central axis and re-rolled around a pipette, resulting in a new billet (non-compressed). The new billet is re-extruded at the same conditions as used during first extrusion process. This step is added to provide advantageous cross-directional mechanical properties to the PTFE tape. Calendaring is performed at 30°C targeting a tape thickness of 9 - 10 mils and cut into 4x4". The resulting tape is then dried at 125 °C for 1 h, whereby the lubricant is removed from the extruded tape.

30 **[0032]** The tape is then stretched at the following conditions: Stretch ratio of machine direction (MD) and transverse direction (TD) is 3 at 300%/sec stretch rate. Temperature in the stretch oven is set to 150 °C.

**[0033]** The stretched tape is then annealed. Annealing is conducted in the annealing oven at 350 °C for 5 sec, following which the tape is cooled. The porosity that is produced by the above stretching steps is retained upon cooling.

**[0034]** Optionally, the porous membrane obtained above is reacted with an acid.

35 **[0035]** In accordance with an embodiment of the invention, the hydrophilic porous PTFE membrane is a porous membrane, e.g., a nanoporous membrane, for example, a membrane having pores of diameter between 1 nm and 100 nm, or a microporous membrane having pores of diameter between 1 μm and 10 μm.

**[0036]** The surface tension of the resulting porous membrane can be determined as follows. For example, a sheet of PTFE porous support is coated at room temperature by prewetting the membrane sheet with IPA solvent and soaking the membrane in a coating polymer solution with concentration that ranges between 0.1% and 10% by mass. The coating time ranges between (1 min to 12 hours). After soaking the support, it is dried in convection oven at 100 °C to 160 °C. The drying time ranges between (10 minutes to 12 h). The resulting porous PTFE membrane's wetting characteristics are measured by measuring the critical wetting surface tension.

40 **[0037]** The change in surface modification in terms of surface tension was measured by measuring the critical wetting surface tension (CWST). The method relies on a set of solutions of certain composition. Each solution has specific surface tension. The solution's surface tension ranges from 25 to 92 dyne/cm in small non-equivalent increments. To measure the membrane surface tension, the membrane is positioned on top of white light table, one drop of a solution of certain surface tension is applied to the membrane surface and the time the drop takes to penetrate through the membrane and become bright white as an indication of light going through the membrane is recorded. Instant wetting is considered when the time the drop takes to penetrate the membrane is ≤ 10 seconds. If the time > 10 seconds, the solution is considered to partially wet the membrane.

45 **[0038]** Hydrophilic porous PTFE membranes according to embodiments of the invention can be used in a variety of applications, including, for example, diagnostic applications (including, for example, sample preparation and/or diagnostic lateral flow devices), ink jet applications, lithography, e.g., as replacement for HD/UHMW PE based media, filtering fluids

for the pharmaceutical industry, metal removal, production of ultrapure water, treatment of industrial and surface waters, filtering fluids for medical applications (including for home and/or for patient use, e.g., intravenous applications, also including, for example, filtering biological fluids such as blood (e.g., virus removal)), filtering fluids for the electronics industry (e.g., filtering photoresist fluids in the microelectronics industry and hot SPM), filtering fluids for the food and beverage industry, beer filtration, clarification, filtering antibody- and/or protein-containing fluids, filtering nucleic acid-containing fluids, cell detection (including *in situ*), cell harvesting, and/or filtering cell culture fluids. Alternatively, or additionally, the porous membranes according to embodiments of the invention can be used to filter air and/or gas and/or can be used for venting applications (e.g., allowing air and/or gas, but not liquid, to pass therethrough). Porous membranes according to embodiments of the inventions can be used in a variety of devices, including surgical devices and products, such as, for example, ophthalmic surgical products.

**[0039]** In accordance with embodiments of the invention, the hydrophilic porous PTFE membrane can have a variety of configurations, including planar, flat sheet, pleated, tubular, spiral, and hollow fiber.

**[0040]** Hydrophilic porous PTFE membranes according to embodiments of the invention are typically disposed in a housing comprising at least one inlet and at least one outlet and defining at least one fluid flow path between the inlet and the outlet, wherein at least one inventive membrane or a filter including at least one inventive membrane is across the fluid flow path, to provide a filter device or filter module. In an embodiment, a filter device is provided comprising a housing comprising an inlet and a first outlet, and defining a first fluid flow path between the inlet and the first outlet; and at least one inventive membrane or a filter comprising at least one inventive membrane, the inventive membrane or filter comprising at least one inventive membrane being disposed in the housing across the first fluid flow path.

**[0041]** Preferably, for crossflow applications, at least one inventive porous membrane or filter comprising at least one inventive membrane is disposed in a housing comprising at least one inlet and at least two outlets and defining at least a first fluid flow path between the inlet and the first outlet, and a second fluid flow path between the inlet and the second outlet, wherein the inventive membrane or filter comprising at least one inventive membrane is across the first fluid flow path, to provide a filter device or filter module. In an illustrative embodiment, the filter device comprises a crossflow filter module, the housing comprising an inlet, a first outlet comprising a concentrate outlet, and a second outlet comprising a permeate outlet, and defining a first fluid flow path between the inlet and the first outlet, and a second fluid flow path between the inlet and the second outlet, wherein at least one inventive membrane or filter comprising at least one inventive membrane is disposed across the first fluid flow path.

**[0042]** The filter device or module may be sterilizable. Any housing of suitable shape and providing an inlet and one or more outlets may be employed.

**[0043]** The housing can be fabricated from any suitable rigid impervious material, including any impervious thermoplastic material, which is compatible with the fluid being processed. For example, the housing can be fabricated from a metal, such as stainless steel, or from a polymer, e.g., transparent or translucent polymer, such as an acrylic, polypropylene, polystyrene, or a polycarbonate resin.

**[0044]** The present invention further provides a hydrophilically modified porous PTFE membrane produced by the method described above.

**[0045]** The present invention further provides a method of filtering a fluid, the method comprising passing the fluid through the hydrophilic porous PTFE membranes described above.

**[0046]** The following examples further illustrate the invention.

#### EXAMPLE 1

**[0047]** This example illustrates a method of preparing a hydrophilic porous PTFE membrane in accordance with an embodiment of the invention.

**[0048]** 200 g of PTFE resin powder, FLUON CD123, was mixed with the desired amounts of the copolymer (PF8PO)<sub>100</sub>-r-(TBGE)<sub>200</sub> in acetone solvent (25%) and Isopar G lubricant (50%) to obtain a blend containing 5% or 10% copolymer. The blend was mixed in a twin roller. The blend was formed into a billet by applying a pressure of 300 psi, at least twice, each for a period of about 55 sec. The resulting billets were equilibrated at room temperature for about 12 hrs. The billets were then extruded through a 26 mm die at the maximum pressure and constant temperature of 55 °C, resulting in a tube-shaped PTFE tape. The tube-shaped tape was cut open along the central axis (along its length) and rolled around a pipette, resulting in a new billet (non-compressed). The new billet was extruded at the same conditions as used during the first extrusion process. Calendaring was performed at 30 °C targeting a tape thickness of 9 - 10 mils and cut into 4x4". The resulting tape was dried at 125 °C for 1 h, whereby the lubricant was removed from the tape. The tape was stretched in the machine direction and the transverse direction with a MD/TD ratio of 3 at a stretch rate of 300%/sec. The temperature of the stretch oven was set at 150 °C. The resulting membrane was annealed in an annealing oven at 150 °C or 350 °C for various times as set forth in Table 2. The membrane performance characteristics are set forth in Table 2, and the results of exposure to formic acid (FA), sulfuric acid (SA), and trifluoroacetic acid (TFA) are set forth in Table 3.

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Table 2. Membrane Preparation Conditions and CWST values

Conditions - Stretch at 150°C and anneal	CWST (Dyne/cm)	Comments
PEO copolymer 2X4 stretch hold at 150C for 30 sec	37-39	Sample appeared to dewet during WF testing
PEO copolymer 2X4 stretch hold for 250C for 30 sec	33-35	Sample appeared to dewet during WF testing
PEO copolymer 2X4 stretch hold at 350C for 30 sec	30-33	Sample appeared to dewet during WF testing
Standard PTFE	25-27	

Table 3. Membrane Performance Characteristics

Conditions	Thickness (mils)	IPA KL (psi)	Water Flow (L/min/ft2/psid)	CWST (Dynes/cm2)
Sample A' 10 phr 2X4 stretch hold at 150 °C for 30 sec	7.4	16	1.42	40-44
Sample B' 10 phr 2X4 stretch hold at 250 °C for 30 sec	6.9	18	1.95	35-37
Sample C' 10 phr 2X4 stretch hold at 350 °C for 30 sec	7.6	12	2.84	30-33
Sample A 5 phr 2X4 stretch hold at 150 °C for 30 sec	8	34	0.4	37 - 39
Sample B 5 phr 2X4 stretch hold at 250 °C for 30 sec	7.7	35	0.54	33 - 35
Sample C 5 phr 2X4 stretch hold at 350 °C for 30 sec	8	25	1.4	30 - 33
Reference				
Control 1 2X4 stretch hold at 150 °C for 30 sec	7.4	25	0.73	25 - 27
Control 2 2X4 stretch hold at 250 °C for 30 sec	7.5	22	1.06	25 - 27
Control 3 2X4 stretch hold at 350 °C for 30 sec	7	16	2.22	25 - 27

Table 4. Results of Reaction with Acids

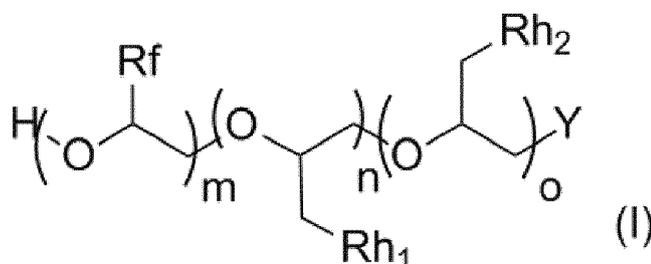
Percentage of amphiphilic copolymer	Sample	CWST On as stretched	CWST after 30 min IPA soak	Post Modification in FA, SA, TFA
5 phr	150 °C for 30 sec	37-40	37-40	-
	250 °C for 30 sec	33-35	33-35	30-33
	350 °C for 30 sec	30-33	30-33	30-33
10 phr	150 °C for 30 sec	40-44	40-44	
	250 °C for 30 sec	35-37	35-37	
	350 °C for 30 sec	30-33	30-33	

### Claims

1. A method of preparing a hydrophilic porous PTFE membrane comprising:

- (i) preparing a blend comprising PTFE and an amphiphilic copolymer, and optionally a lubricant;
- (ii) extruding the blend into a tape;
- (iii) biaxially stretching the tape to obtain a hydrophilic porous membrane;

wherein the amphiphilic copolymer is of formula (I):



wherein the amphiphilic copolymer is a random or block copolymer, Rf is a perfluoro-substituted group, wherein Rh<sub>1</sub> and Rh<sub>2</sub> are hydrophilic groups independently selected from hydroxyl, acyloxy, trifluoroacetyl, alkyloxy, allyloxy, alkylthio, and alkylthiopropoxy, or chlorine, wherein the alkyl portion of alkylthio and alkylthiopropoxy are optionally substituted with hydroxyl, carboxylic acid, sulfonic acid, phosphonic acid, quaternary ammonium, alkylsulfonyl, heterocyclyl;

m and n are independently from 10 to 1000, and o is from 0 to 1000;  
Y is hydroxyl.

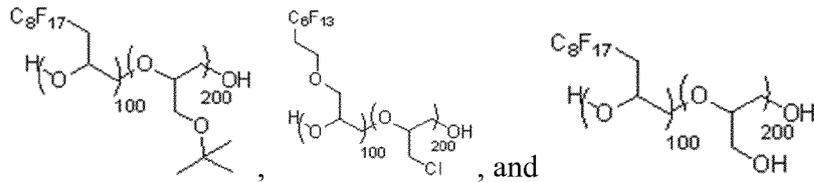
2. The method of claim 1 comprising (iv) annealing the hydrophilic porous membrane.

3. A hydrophilic porous membrane obtainable by the method of claim 1 or 2.

4. The hydrophilic porous membrane of claim 3, wherein Rf is a perfluoro-substituted alkyl, wherein the alkyl chain may optionally contain one or more oxygen atoms in the chain.

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5. The hydrophilic porous membrane of claim 3 or 4, wherein Rf is  $C_pF_{2p+1}(CH_2)_q(OCH_2)_r$ , wherein p is 1 to 12, q is 0 to 3, and r is 0 to 2.
6. The hydrophilic porous membrane of claim 5, wherein Rf is independently selected from  $C_8F_{17}CH_2$ ,  $C_6F_{13}(CH_2)_2OCH_2$ ,  $C_4F_9CH_2$  and  $CF_3$ .
7. The hydrophilic porous membrane of claim 6, wherein Rf is selected from  $C_8F_{17}CH_2$  and  $C_6F_{13}(CH_2)_2OCH_2$ .
8. The hydrophilic porous membrane of any one of claims 3 to 7, wherein Rh<sub>1</sub> and Rh<sub>2</sub> are selected from hydroxyl and trifluoroacetyl.
9. The hydrophilic porous membrane of claim 3, wherein the amphiphilic copolymer is selected from:



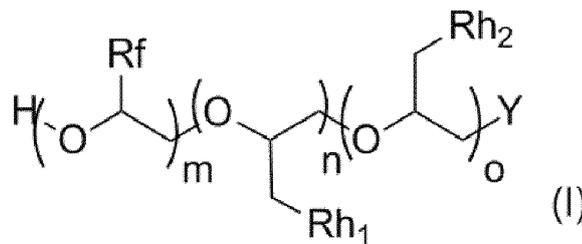
10. A method of filtering a fluid, the method comprising passing the fluid through the hydrophilic porous membrane of any one of claims 3 to 9.

Patentansprüche

1. Verfahren zur Herstellung einer hydrophilen porösen PTFE-Membran, umfassend:

- (i) Herstellen einer Mischung, welche PTFE und ein amphiphiles Copolymer und optional ein Gleitmittel umfasst;  
 (ii) Extrudieren der Mischung zu einem Band;  
 (iii) biaxiales Strecken des Bandes, um die hydrophile poröse Membran zu erhalten;

wobei das amphiphile Copolymer die Formel (I) aufweist:



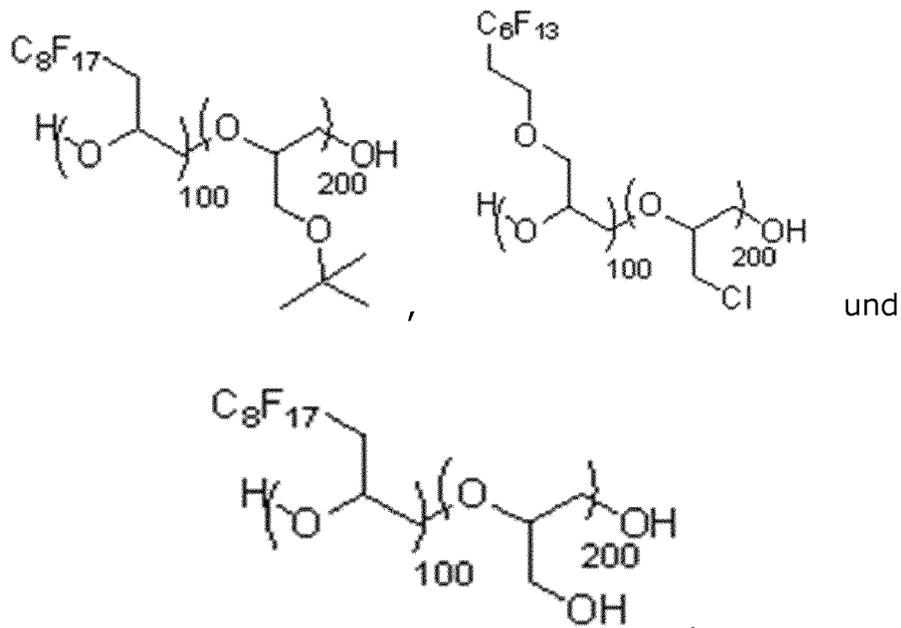
worin das amphiphile Copolymer ein Random- oder ein Block-Copolymer ist, worin Rf eine perfluorsubstituierte Gruppe ist, worin Rh<sub>1</sub> und Rh<sub>2</sub> hydrophile Gruppen sind, welche unabhängig voneinander ausgewählt sind aus Hydroxyl, Acyloxy, Trifluoroacetyl, Alkyloxy, Allyloxy, Alkylthio und Alkylthiopropoxy oder Chlor, wobei der Alkylteil von Alkylthio und Alkylthiopropoxy optional substituiert ist mit Hydroxyl, Carbonsäure, Sulfonsäure, Phosphonsäure, quaternärem Ammonium, Alkylsulfonyl, Heterocyclyl;

m und n unabhängig voneinander eine Zahl von 10 bis 1000 sind und o eine Zahl von 0 bis 1000 ist; Y Hydroxyl ist.

2. Verfahren nach Anspruch 1, umfassend: (iv) Wärmebehandeln der hydrophilen porösen Membran.
3. Hydrophile poröse Membran, erhältlich nach dem Verfahren von Anspruch 1 oder 2.
4. Hydrophile poröse Membran nach Anspruch 3, wobei Rf ein perfluorsubstituiertes Alkyl ist, wobei die Alkylkette optional ein oder mehrere Sauerstoffatome in der Kette enthalten kann.

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5. Hydrophile poröse Membran nach Anspruch 3 oder 4, wobei  $R_f$   $C_pF_{2p+1}-(CH_2)_q(OCH_2)_r$  ist, worin  $p$  1 bis 12 ist, worin  $q$  0 bis 3 ist und worin  $r$  0 bis 2 ist.
6. Hydrophile poröse Membran nach Anspruch 5, wobei  $R_f$  unabhängig ausgewählt ist aus  $C_8F_{17}CH_2$ ,  $C_6F_{13}(CH_2)_2OCH_2$ ,  $C_4F_9CH_2$  und  $CF_3$ .
7. Hydrophile poröse Membran nach Anspruch 6, wobei  $R_f$  ausgewählt ist aus  $C_8F_{17}CH_2$  und  $C_6F_{13}(CH_2)_2OCH_2$ .
8. Hydrophile poröse Membran nach einem der Ansprüche 3 bis 7, wobei  $R_{h1}$  und  $R_{h2}$  ausgewählt sind aus Hydroxyl und Trifluoracetyl.
9. Hydrophile poröse Membran nach Anspruch 3, wobei das amphiphile Copolymer ausgewählt ist aus:



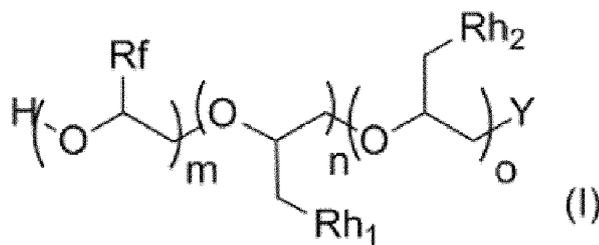
10. Verfahren zum Filtern eines Fluids, wobei das Verfahren ein Durchleiten des Fluids durch die hydrophile poröse Membran nach einem der Ansprüche 3 bis 9 umfasst.

Revendications

1. Procédé de préparation d'une membrane de PTFE poreuse hydrophile comprenant :

- (i) la préparation d'une combinaison comprenant PTFE et un copolymère amphiphile, et éventuellement un lubrifiant ;
- (ii) l'extrusion de la combinaison en une bande ;
- (iii) l'étirage biaxial de la bande pour obtenir une membrane poreuse hydrophile ;

dans lequel le copolymère amphiphile est de formule (I) :

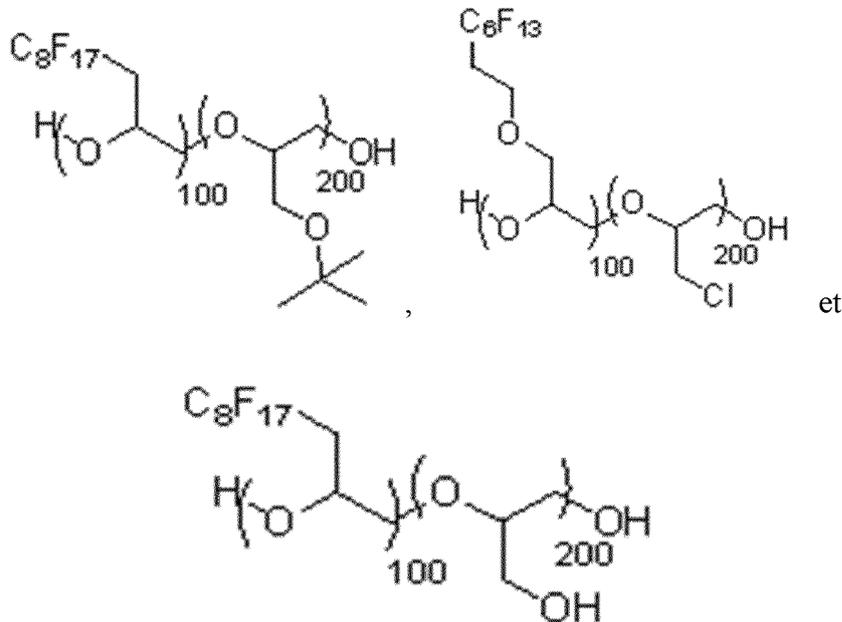


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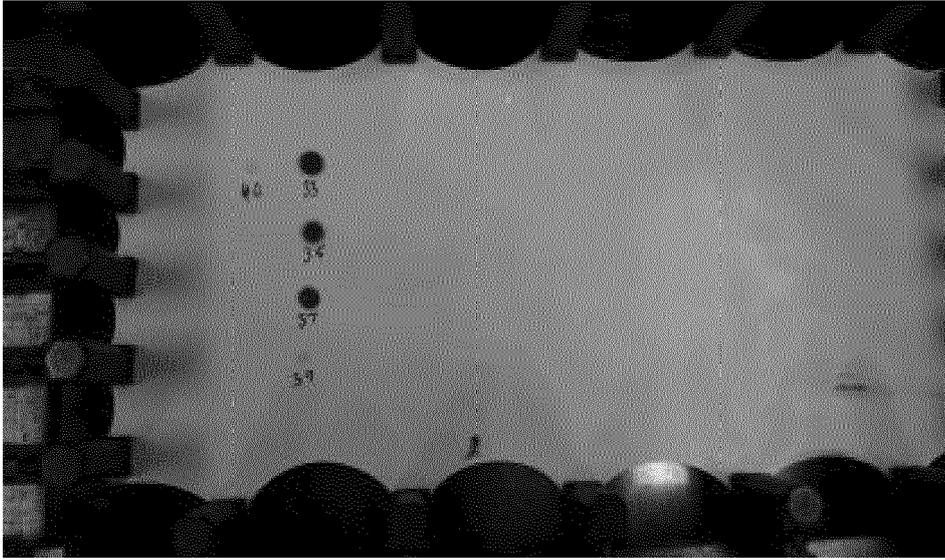
dans lequel le copolymère amphiphile est un copolymère aléatoire ou séquencé, Rf est un groupe perfluoro-substitué, dans lequel Rh<sub>1</sub> et Rh<sub>2</sub> sont des groupes hydrophiles indépendamment choisis parmi un groupe hydroxyle, acyloxy, trifluoroacétyle, alkyloxy, allyloxy, alkylthio, et alkylthiopropoxy, ou chlore, dans lequel la portion alkyle du groupe alkylthio et alkylthiopropoxy est éventuellement substituée avec un groupe hydroxyle, acide carboxylique, acide sulfonique, acide phosphonique, ammonium quaternaire, alkylsulfonyle, hétérocyclyle,

m et n sont indépendamment de 10 à 1 000, et o est de 0 à 1 000 ;  
Y est le groupe hydroxyle.

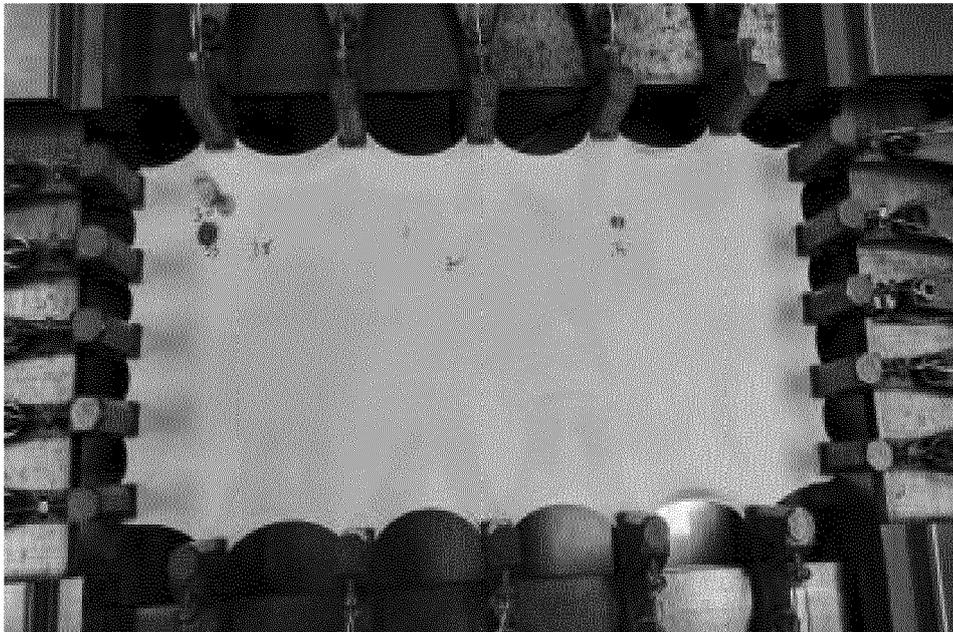
2. Procédé selon la revendication 1 comprenant (iv) le recuit de la membrane poreuse hydrophile.
3. Membrane poreuse hydrophile pouvant être obtenue par le procédé de la revendication 1 ou 2.
4. Membrane poreuse hydrophile selon la revendication 3, dans laquelle Rf est un groupe alkyle perfluoro-substitué, dans laquelle la chaîne alkyle peut éventuellement contenir un ou plusieurs atomes d'oxygène dans la chaîne.
5. Membrane poreuse hydrophile selon la revendication 3 ou 4, dans laquelle Rf est C<sub>p</sub>F<sub>2p+1</sub>-(CH<sub>2</sub>)<sub>q</sub>(OCH<sub>2</sub>)<sub>r</sub>, dans laquelle p est de 1 à 12, q est de 0 à 3, et r est de 0 à 2.
6. Membrane poreuse hydrophile selon la revendication 5, dans laquelle Rf est indépendamment choisi parmi C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>, C<sub>6</sub>F<sub>13</sub>(CH<sub>2</sub>)<sub>2</sub>OCH<sub>2</sub>, C<sub>4</sub>F<sub>9</sub>CH<sub>2</sub> et CF<sub>3</sub>.
7. Membrane poreuse hydrophile selon la revendication 6, dans laquelle Rf est choisi parmi C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub> et C<sub>6</sub>F<sub>13</sub>(CH<sub>2</sub>)<sub>2</sub>OCH<sub>2</sub>.
8. Membrane poreuse hydrophile selon l'une quelconque des revendications 3 à 7, dans laquelle Rh<sub>1</sub> et Rh<sub>2</sub> sont choisis parmi le groupe hydroxyle et trifluoroacétyle.
9. Membrane poreuse hydrophile selon la revendication 3, dans laquelle le copolymère amphiphile est choisi parmi :



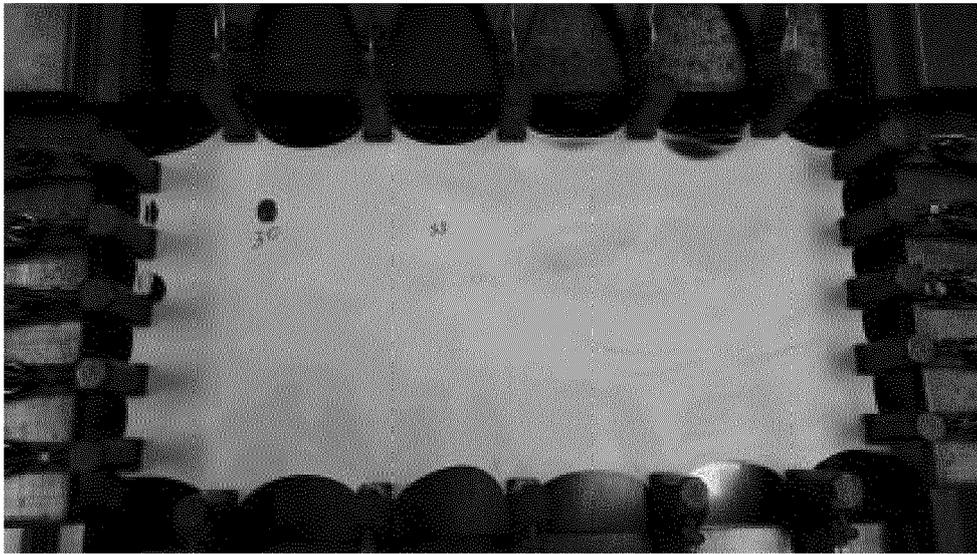
10. Procédé de filtration d'un fluide, le procédé comprenant le passage du fluide à travers la membrane poreuse hydrophile selon l'une quelconque des revendications 3 à 9.



**FIG. 1**



**FIG. 2**



**FIG. 3**

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

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**Non-patent literature cited in the description**

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