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(54) **Title:** GAS-SEPARATION MEMBRANES

(57) **Abstract:** A gas-separation membrane comprising the following components: (i) a porous substrate; and (ii) a discriminating layer in contact with the porous substrate; wherein the discriminating layer is obtainable by curing a composition comprising a curable copolymer, wherein the curable copolymer comprises m epoxide groups and n polyethylene oxide) groups of the formula $-(CH_2CH_2O)_q-$; wherein: q has a value of 4 to 23; and (m+n) has a value of 550 to 2,600.

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GAS-SEPARATION MEMBRANES

This invention relates to gas-separation membranes (GSMs) and to their preparation and use.

For purifying gaseous mixtures e.g. natural gas and flue gas, the removal of undesired components can in some cases be achieved based on the relative size of the components (size-sieving).

US 8,177,891 describes GSMs comprising a continuous substantially non-porous layer comprising the polymerization product of a compound, which compound comprises at least 70 oxyethylene groups forming an uninterrupted chain of the formula $-(CH_2CH_2O)_n-$ wherein n is at least 70.

US 8,303,691 describes composite membranes comprising a polymer sheet and a porous support layer for the polymer sheet, characterised in that the polymer sheet comprises at least 60wt% of oxyethylene groups and the porous support layer has defined flux properties.

US 8,034,444 describes a porous membrane obtainable by polymerizing at least one type of curable epoxy acrylate monomer that is soluble in a solvent wherein at least 50 wt % of said solvent is water.

There is a need for strong, flexible GSMs having a high permeability and being capable of discriminating well between gases (e.g. between polar and non-polar gases). Ideally such membranes can be produced efficiently at high speeds using toxicologically acceptable liquids (particularly water). In this manner the membranes could be made in a particularly cost effective manner.

According to a first aspect of the present invention there is provided a gas-separation membrane comprising the following components:

(i) a porous substrate; and

(ii) a discriminating layer in contact with the porous substrate;

wherein the discriminating layer is obtainable by curing a composition comprising a curable copolymer, wherein the curable copolymer comprises m epoxide groups and n poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q-$;

wherein:

q	has a value of 4 to 23; and
(m+n)	has a value of 550 to 2,600.

In this specification the term “comprising” is to be interpreted as specifying the presence of the stated parts, steps or components, but does not exclude the presence of one or more additional parts, steps or components.

Reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element(s) is present, unless the context

clearly requires that there be one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

In this specification the curable copolymer comprising m epoxide groups and n poly(ethylene oxide) groups is often abbreviated to the “curable copolymer”.

Preferably the curable copolymer has a numbered averaged molecular weight (NAMW) in the range 360 kDa to 1500 kDa, more preferably in the range 360 kDa to 1200 kDa and especially in the range 400 kDa to 1000 kDa. The NAMW may be determined by gel permeation chromatography, e.g. as described below in more detail.

The value of m defines the number of epoxide groups present in the curable copolymer and thereby influences the degree to which the discriminating layer is crosslinked. m preferably has a value of 100 to 500, more preferably 200 to 400.

The value of n defines the number of poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q-$ (wherein q is as hereinbefore defined) present in the curable copolymer and thereby affects the polarity of the discriminating layer. n preferably has a value of 500 to 1,200, more preferably 600 to 1,000.

In our experiments we observed that the value of (m+n) can influence how much of the curable copolymer is impregnated into the porous substrate and how much will stay on top of the porous substrate to form a discriminating layer external to the porous substrate. On the one hand, when the value of (m+n) is below 550, the curable copolymer will usually fully impregnate into the porous substrate without leaving any observable discriminating layer on top of the porous substrate. As a result, the GSM can have performance shortcomings as described in more detail below in relation to the dying test. On the other hand, when the value of (m+n) is above 2,600, the curable copolymer impregnates the porous substrate little or not at all. As a consequence the resultant discriminating layer is entirely or almost entirely on top of the porous substrate and the bond between the discriminating layer and the porous substrate may, as a result, be weak. However when the value of (m+n) is from 550 to 2,600, the curable copolymer partially impregnates the substrate and on curing a discriminating layer is formed on top of and to some extent within the porous substrate leading to GSMs having advantageous properties.

Preferably the value of (m+n) is in the range 750 to 2,000, more preferably in the range 900 to 1,500.

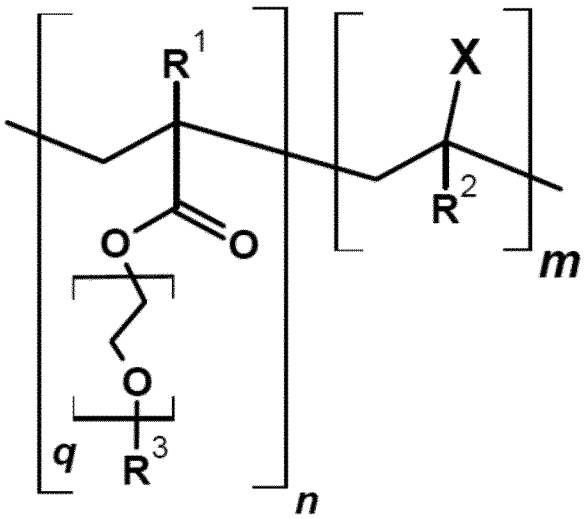
The values of m and n are integers above 1.

The polarity of the discriminating layer is important for achieving good separation of polar and non-polar gases, e.g. for the removal of H_2S from mixed gas streams.

The value of q also influences the polarity of the discriminating layer, with higher values of q resulting in membranes of higher polarity. Preferably q has a value of 6 to 20, more preferably 9 to 18. When q has a value above 23 crystallisation of

poly(ethylene glycol) in the discriminating layer can occur which adversely affects the performance of the GSM.

Preferably the curable copolymer comprises a group of Formula (1):



Formula (1)

wherein m, n, q and (m+n) are as defined above (with preferences defined above);

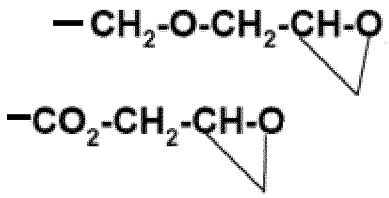
X is an epoxide-containing group;

each R^1 and R^2 independently is H or an optionally substituted alkyl group; and

R^3 is H or an optionally substituted alkyl or an optionally substituted phenyl group.

In addition to an epoxide group, X preferably further comprises at least one methylene (-CH_2-) group and optionally one or more groups selected from ester groups (e.g. -CO_2-) and ether (-O-) groups. For example X may be of the formula –$(CH_2)_{t1}$-O-$(CH_2)_{t2}$-$CHCH_2O$, –$(CH_2)_{t1}$-(O-$CH_2)_{t2}$-$CHCH_2O$ or –CO_2-$(CH_2)_{t1}$-$CHCH_2O$ wherein t1 and t2 each independently have a value of from 1 to 4, more preferably 1 (-$CHCH_2O$ is an epoxide group).

Specific examples of groups represented by X and include a terminal epoxide group include the following:



When R^1, R^2 or R^3 is an optionally substituted alkyl group it is preferably an optionally substituted C_{1-4}-alkyl group.

The optional substituents which may be present in R^1, R^2 or R^3 are preferably selected from epoxide, C_{1-4}-alkyl, C_{1-4}-alkoxy, sulpho, carboxy and hydroxyl groups.

The amount of curable copolymer present in the composition used to form the discriminating layer is preferably in the range of 1 to 25wt%, more preferably 5 to 15wt%, relative to the weight of the composition.

The composition used to form the discriminating layer optionally comprises a crosslinking agent (in addition to the curable copolymer), especially a crosslinking agent comprising two or more groups selected from epoxide groups and particularly ethylenically unsaturated groups.

Preferred ethylenically unsaturated groups include allyl groups and (meth)acrylic groups (e.g. $CH_2=CR^4$-C(O)- groups), especially (meth)acrylate groups (e.g. $CH_2=CR^4$-C(O)O- groups) and (meth)acrylamide groups (e.g. $CH_2=CR^4$-C(O)NR^4- groups), wherein each R^4 independently is H or CH_3.

Examples of crosslinking agents for the curable copolymer which comprise epoxide groups include, for example, poly(ethylene glycol) diglycidyl ether, polyglycidyl ether cyclosiloxane, resorcinol diglycidyl ether, N,N-diglycidyl-4-glycidyloxyaniline, bisphenol A propoxylate diglycidyl ether, and trimethylolpropane triglycidyl ether poly(ethylene glycol) diacrylate, glycidyl methacrylate bisphenol A ethoxylate diacrylate, neopentyl glycol ethoxylate (di)acrylate, propanediol ethoxylate diacrylate, butanediol ethoxylate diacrylate, hexanediol ethoxylate diacrylate and combinations of two or more thereof.

Examples of crosslinking agents for the curable copolymer which do not comprising epoxide groups include, for example, compounds comprising two or more groups which are reactive with epoxide groups, for example two or more groups selected from carboxylic acid, hydroxyl, thiol and/or anhydride groups, for example (cyclo)aliphatic or aromatic di-, tri- or poly-carboxylic acids, e.g. succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, trimesic acid; (cyclo)aliphatic or aromatic di-, tri- or poly-thiols, e.g. 1,2-ethanedithiol, 1,4-butanedithiol, 1,6-hexanedithiol, benzene-1,2-dithiol, benzene-1,3-dithiol, benzene-1,4-dithiol, 1,2-benzenedimethanethiol, 1,3-benzenedimethanethiol, 1,4-benzenedimethanethiol or toluene-3,4-dithiol; (cyclo)aliphatic or aromatic di-, tri- or poly-amines, e.g. ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, cadaverine, hexamethylenediamine, 1,8-diaminooctane, 1,2-bis(3-aminopropylamino)ethane, 1,2-diaminocyclohexane, 4-aminobenzylamine, o-xylylenediamine, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine; or (cyclo)aliphatic or aromatic anhydrides, e.g. succinic anhydride, 3,3-dimethylglutaric anhydride, ethylenediaminetetraacetic dianhydride, glutaric anhydride, phenylsuccinic anhydride, pyromellitic dianhydride, or phthalic anhydride; metal alkoxides, e.g. alkoxides of zirconium, titanium or niobium, especially titanium (IV) isopropoxide,

titanium (IV) ethoxide, zirconium propoxide and/or niobium ethoxide. Preferably the crosslinking agent comprises two (i.e. two and not more than two) reactive groups.

The amount of crosslinking agent present in the composition used to form the discriminating layer is preferably in the range of 0 to 30wt%, more preferably 0.1 to 30wt%, especially 0.5 to 20wt%, and more especially than 10wt%, relative to the weight of the composition.

The composition used to form the discriminating layer optionally further comprises a monomer having only one group which is reactive with the curable copolymer. Examples of such further monomers include alkyl glycidyl ether, bisphenol A (2,3-dihydroxypropyl) glycidyl ether, glycidyl acrylate, glycidyl methacrylate bisphenol A ethoxylate (di)acrylate, neopentyl glycol ethoxylate (di)acrylate, propanediol ethoxylate (di)acrylate, butanediol ethoxylate (di)acrylate, hexanediol ethoxylate (di)acrylate

The amount of such further monomers having only one group which is reactive with the curable copolymer present in the composition used to form the discriminating layer is preferably in the range of 0 to 30wt%, more preferably 0 to 20wt%, and especially 0 to 5wt%, relative to the weight of the composition.

Preferably the composition used to form the discriminating layer comprises an inert solvent. Inert solvents are not curable and do not cross-link with any component of the composition.

Examples of inert solvents include alcohol-based solvents, ether-based solvents, amide-based solvents, ketone-based solvents, sulfoxide-based solvents, sulfone-based solvents, nitrile-based solvents and organic phosphorus-based solvents. Examples of alcohol-based solvents include methanol, ethanol, isopropanol, n-butanol, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol and mixtures comprising two or more thereof.

Examples of inert solvents include dimethyl sulfoxide, dimethyl imidazolidinone, sulfolane, N-methyl pyrrolidone, dimethyl formamide, acetonitrile, acetone, 1,4-dioxane, 1,3-dioxolane, tetramethyl urea, hexamethyl phosphoramide, hexamethyl phosphorotriamide, pyridine, propionitrile, butanone, cyclohexanone, tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran, ethylene glycol diacetate, cyclopentylmethylether, methylethylketone, ethyl acetate, y-butyrolactone and mixtures comprising two or more thereof. Dimethyl sulfoxide, N-methyl pyrrolidone, dimethyl formamide, dimethyl imidazolidinone, sulfolane, acetone, cyclopentylmethylether, methylethylketone, acetonitrile, tetrahydrofuran, 2-methyltetrahydrofuran and mixtures comprising two or more thereof.

Preferably the composition used to prepare the discriminating layer is free from water, even when the curable copolymer is water-soluble. However if necessary one may include water in the composition as part of the inert solvent, preferably 10 wt% or

less, more preferably 5 wt% or less and most preferably 0 wt%, relative to the total weight of inert solvent present in the composition. Surprisingly omitting water from the composition used to form the discriminating layer results in fewer defects in the resultant discriminating layer.

Especially preferred inert solvents include methyl ether ketone, n-butyl acetate, ethyl acetate, cyclopentyl methyl ether and 2-methyltetrahydrofuran.

The inert solvent optionally comprises a single inert solvent or a combination of two or more inert solvents. Preferred inert solvents include C_{1-4} alcohols (e.g. methanol, ethanol and propan-2-ol), diols (e.g. ethylene glycol and propylene glycol), triols (e.g. glycerol), carbonates (e.g. ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, di-t-butyl dicarbonate and glycerin carbonate), dimethyl formamide, acetone, methyl ethyl ketone, ethyl acetate, butyl acetate, 2-methyl tetrahydrofuran, cyclopentyl methyl ether, N-methyl-2-pyrrolidinone and mixtures comprising two or more thereof. A particularly preferred inert solvent is n-butyl acetate, methyl ethyl ketone or ethyl acetate. In one embodiment the inert solvent has a low boiling point e.g. a boiling point below 100°C. Solvents having a low boiling point can be easily removed after curing by evaporation, avoiding the need for a washing step for removal of the solvent.

Being inert, the solvent does not co-polymerize with any of the other components of the composition.

The amount of inert solvent present in the composition used to form the discriminating layer is preferably in the range of 40 to 99wt%, more preferably 50 to 90wt%,, relative to the weight of the composition

Preferably the composition used to form the discriminating layer comprises a surfactant, e.g. 0.1 to 5wt% and especially 0.2 to 2wt% of surfactant, relative to the total weight of the composition.

Preferred surfactants are ionic and non-ionic surfactants, for example ethoxylated and alkoxylated fatty acids, ethoxylated amines, ethoxylated alcohol, alkyl and nonyl-phenol ethoxylates, ethoxylated sorbitan esters, and EO/PO copolymers, in which EO is ethylene oxide and PO is propylene oxide . The most preferred surfactant is a polyether-modified acryl functional polydimethylsiloxane (available as UV-3530 from Byk). Optionally the composition used to form the discriminating layer comprises one or more further adjuvents, binders, etc. (e.g. in an amount of up to 1.0wt% %, relative to the total weight of the composition).

The curing will provide cross-linking of the curable copolymer via cationic ring-opening polymerization of the glycidyl functionalities to obtain the selective layer or discriminating layer on top of the porous substrate.

The composition used to form the discriminating layer preferably further comprises an initiator which facilitates curing of the polymerisable components present

in the composition. Any initiator capable of polymerizing a polyepoxide may be used, e.g. a thermal initiator, photo-initiator a Lewis acid and/or a Lewis base. The initiator may be anionic, cationic or neutral. Also the curing may comprise inter- and/or intra-molecular polymerization.

Photo-initiators are usually required when the curing uses light, for example ultraviolet ("UV") light.

Preferred photo-initiators for use in cationic UV cure include, but are not limited to organic salts of non-nucleophilic anions, e.g. hexafluoroarsinate anion, antimony (V) hexafluoride anion, phosphorus hexafluoride anion, tetrafluoroborate anion and tetrakis (2,3,4,5,6-pentafluorophenyl)boranuide anion, (4-phenylthiophenyl)diphenylsulfonium triflate; triphenylsulfonium triflate; Irgacure(R) 270 (available from BASF); triarylsulfonium hexafluoroantimonate; triarylsulfonium hexafluorophosphate; CPI-100P (available from SAN-APRO); CPI-210S (available from SAN-APRO) and especially Irgacure(R) 290 (available from BASF), CPI-100P from San-Apro Limited of Japan, triphenylsulphonium hexafluorophosphate, triphenylsulphonium hexafluoroantimonate, triphenylsulphonium tetrakis(pentafluorophenyl)borate, 4,4'-bis[diphenylsulphonio]diphenylsulfide bishexafluorophosphate, 4,4'-bis[di(beta-hydroxyethoxy)phenylsulphonio]diphenylsulfide bishexafluoroantimonate, 4,4'-bis[di(beta-hydroxyethoxy)phenylsulphonio]diphenylsulfide bishexafluorophosphate, 7-[di(p-toluyl)sulphonio]-2-isopropylthioxanthone hexafluoroantimonate, 7-[di(p-toluyl)sulphonio]-2-isopropylthioxanthone tetrakis(pentafluorophenyl)borate, 4-phenylcarbonyl-4'-diphenylsulphonio-diphenylsulphide hexafluorophosphate, 4-(p-tert-butylphenylcarbonyl)-4'-diphenylsulphonio-diphenylsulphide hexafluoroantimonate, and 4-(p-tert-butylphenylcarbonyl)-4'-di(p-toluyl)sulphonio-diphenylsulphide tetrakis(pentafluorophenyl)borate (e.g. DTS-102, DTS-103, NDS-103, TPS-103, MDS-103 from Midori Chemical Co. Ltd.), phenyliodonium hexafluoroantimonate (e.g. CD-1012 from Sartomer Corp.), diphenyliodonium tetrakis(pentafluorophenyl)borate, diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, bis(dodecylphenyl)iodonium hexafluoroantimonate, and di(4-nonylphenyl)iodonium hexafluorophosphate, MPI-103, BBI-103 from Midori Chemical Co. Ltd., certain iron salts (e.g. IrgacureTM 261 from Ciba), 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl) borate ((C40H18BF20I)) available under the name I0591 from TCI) and 4-(octyloxy)phenyl](phenyl) iodonium hexafluoroantimonate (C20H26F6IOSb, available as AB153366 from ABCR GmbH Co).

Especially preferred initiators include organic salts of non-nucleophilic anions, e.g. hexafluoroarsinate anion, antimony (V) hexafluoride anion, phosphorus hexafluoride anion, tetrafluoroborate anion and tetrakis(2,3,4,5,6-pentafluorophenyl) boranide anion. Commercially available cationic photo-initiators include UV-9380c, UV-9390c (manufactured by Momentive performance materials), UVI-6974, UVI-6970,

UVI-6990 (manufactured by Union Carbide Corp.), CD-1010, CD-1011, CD-1012 (manufactured by Sartomer Corp.), Adekaoptomer™ SP-150, SP-151, SP-170, SP-171 (manufactured by Asahi Denka Kogyo Co., Ltd.), Irgacure™ 250, Irgacure™ 261 (Ciba Specialty Chemicals Corp.), CI-2481, CI-2624, CI-2639, CI-2064 (Nippon Soda Co., Ltd.), DTS-102, DTS-103, NAT-103, NDS-103, TPS-103, MDS-103, MPI-103 and BBI-103 (Midori Chemical Co., Ltd.). The above mentioned cationic photo-initiators can be used either individually or in combination of two or more. Most preferred are sulfonium and iodonium salts.

Ring opening adjuvants include cationic photoinitiators, Lewis acids (e.g.titanium(IV)isopropoxide) and Lewis bases (e.g. Phosphazene bases, e.g. P1-t-Bu-tris(tetramethylene) and/or N,N,N',N'-tetramethylethylenediamine).

A single type of initiator may be used but also a combination of several different types.

Optionally when no initiator is included in the composition used to form the discriminating layer, the composition can be advantageously cured by electron-beam exposure. Preferably the electron beam output is between 50 and 300keV. Curing can also be achieved by plasma or corona exposure.

Preferably the composition used to form the discriminating layer comprises 0 to 8 wt%, more preferably 0.005 to 8wt%, especially 0.01 to 5wt% and more especially 0.1 to 3wt% of initiator.

In view of the foregoing, the composition used to prepare the discriminating layer preferably comprises:

(a) 1 to 25wt%, more preferably 5 to 15wt%, of the curable copolymer;
(b1) 0 to 30wt%, more preferably 0 to 20wt%, of crosslinking agent;
(b2) 0 to 30wt%, more preferably 0 to 20wt%, of a monomer having only one group reactive with the curable copolymer;
(c) 40 to 99wt%, more preferably 50 to 90wt%, of inert solvent;
(d) 0.1 to 5wt%, more preferably 0.2 to 2wt%, of surfactant; and
(e) 0 to 8wt%, more preferably 0.005 to 8wt%, of initiator.

Preferably the amount of (a) + (b1) + (b2) + (c) + (d) + (e) adds up to 100%. This does not exclude the presence of other components other than (a), (b1), (b2), (c), (d) and (e) but it sets the total amount of these four components. In one embodiment the composition consists solely of components (a), (b1), (b2), (c), (d) and (e).

Preferably the composition used to form the discriminating layer is substantially free from (e.g. contains less than 0.1wt%, more preferably less than 0.01wt%) particulate inorganic particles, e.g. substantially free from (e.g. contains less than 0.1wt%, more preferably less than 0.01wt%) inorganic particles of size (diameter) 0.4 to 5.1 μm.

The composition used to form the discriminating layer is preferably free from (e.g. contains less than 0.1wt%, more preferably less than 0.01wt%) zeolites, porous silicas, carbon nanotubes, graphene oxides and/or metal-organic frameworks (MOFs).

In this way, a smooth, homogenous GSM can be obtained.

The composition used to form the discriminating layer may be cured by any suitable technique, for example by thermal curing and/or radiation curing. Suitable radiation curing techniques include curing, gamma rays, x-rays and especially ultraviolet light or an accelerated electron beams. Suitable thermal curing techniques include radiation heating (e.g. infrared, laser and microwave), convection and conduction heating (hot gas, flame, oven and hot shoe), induction heating, ultrasonic heating and resistance heating.

The discriminating layer may be obtained by curing the abovementioned composition.

The discriminating layer preferably has an average thickness in the range 50 to 1,500nm, more preferably 100 to 1,000nm and especially 150 to 800nm, when measured from the surface of the porous substrate outwards.

The curable copolymer comprising m epoxide groups and n poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q$ (wherein m, n and q are as defined above) may be prepared by, for example, copolymerizing a composition comprising the following components:

(i) an ethylenically unsaturated monomer comprising an epoxide group with (often abbreviated herein to “epoxide monomer”); and

(ii) an ethylenically unsaturated monomer comprising a poly(ethylene oxide) group (often abbreviated herein to “PEG monomer”);

optionally (iii) one or more further monomers;

optionally (iv) and inert solvent;

optionally (v) an initiator (especially a thermal initiator); and

optionally (vi) a surfactant.

This copolymerisation is preferably performed using one or more of the following process features:

(a) an elevated temperature, e.g. a temperature in the range 30 to 120 ^{O}C, especially 55 to 95 ^{O}C; and

(b) in the absence of oxygen, e.g. under a blanket of nitrogen; (c) for a period of 2 to 48 hours, especially 10 to 24 hours.

Typical conditions for preparing the curable copolymer are illustrated in the Examples section below. By adjusting the copolymerization time, temperature and the ratio of components (i) and (ii) one may tailor the values of m, n and q as desired.

Preferably the epoxide monomer is free from poly(ethylene oxide) groups.

Preferably the PEG monomer is free from epoxide groups.

Preferred ethylenically unsaturated monomers comprising an epoxide group include glycidyl (meth)acrylate, allyl glycidyl ether, alpha-glycidyl ether, omega-acrylate poly(ethylene glycol) and/ or (3,4-epoxycyclohexyl)methyl (meth)acrylate .

The amount of epoxide monomer present in the composition used to make the curable copolymer is preferably in the range of 0.5 to 25wt%, more preferably 1 to 20wt%, and especially 1 to 15wt%, relative to the weight of the composition.

Preferred ethylenically unsaturated monomers comprising a poly(ethylene oxide) group include methoxy-poly(ethylene glycol) acrylate, poly(ethylene glycol) (di)acrylate, bisphenol A ethoxylate (di)acrylate, neopentyl glycol ethoxylate (di)acrylate, propanediol ethoxylate (di)acrylate, butanediol ethoxylate (di)acrylate, hexanediol ethoxylate (di)acrylate and combinations of two or more thereof.

The amount of PEG monomer present in the composition used to make the curable copolymer is preferably in the range of 10 to 80wt%, more preferably 15 to 60wt%, and especially 20 to 50wt%, relative to the weight of the composition.

Optionally the composition used to prepare the curable copolymer further comprises one or more further monomers, e.g. a crosslinking agent and/or a monomer having only one ethylenically unsaturated group.

Preferred crosslinking agents comprising two or more ethylenically unsaturated groups.

Preferred ethylenically unsaturated groups include allyl groups and (meth)acrylic groups (e.g. $CH_2=CR^4$-C(O)- groups), especially (meth)acrylate groups (e.g. $CH_2=CR^4$-C(O)O- groups) and (meth)acrylamide groups (e.g. $CH_2=CR^4$-C(O)NR^4- groups), wherein each R^4 independently is H or CH_3.

Examples of crosslinking agents include, for example, poly(ethylene glycol) diglycidyl ether, polyglycidyl ether cyclosiloxane, resorcinol diglycidyl ether, N,N-diglycidyl-4-glycidyloxyaniline, bisphenol A propoxylate diglycidyl ether, and trimethylolpropane triglycidyl ether poly(ethylene glycol) diacrylate, glycidyl methacrylate bisphenol A ethoxylate diacrylate, neopentyl glycol ethoxylate (di)acrylate, propanediol ethoxylate diacrylate, butanediol ethoxylate diacrylate, hexanediol ethoxylate diacrylate and combinations of two or more thereof.

Examples of such further monomers having only one ethylenically unsaturated group include poly(ethylene glycol) acrylate, dimethyl(aminopropyl) (meth)acrylamide, allyl (meth)acrylate, vinyl (meth)acrylate or an epoxide monomer other than already used as (i).

The amount of such further monomers which may be included in the composition used to form the curable copolymer is preferably in the range of 0 to

10wt%, more preferably 0 to 5wt%, and especially 0 to 2wt%, relative to the weight of the composition.

The composition used to form the curable copolymer preferably comprises an initiator, e.g. a thermal initiator and/or a photo-initiator.

Examples of suitable thermal initiators include organic peroxides, for example ethyl peroxide and benzyl peroxide; hydroperoxides, e.g. methyl hydroperoxide; acyloins, e.g. benzoin; certain azo compounds, e.g. α,α′-azobisisobutyronitrile and γ,γ′-azobis(γ-cyanovaleric acid); persulfates; peracetates, e.g. methyl peracetate and tert-butyl peracetate; peroxalates, e.g. dimethyl peroxalate and di(tert-butyl) peroxalate; disulfides, e.g. dimethyl thiuram disulfide; and ketone peroxides, e.g. methyl ethyl ketone peroxide. When the precursor polymer composition comprises a thermal initiator curing is preferably performed at a temperature in the range of from about 30°C to about 150°C, especially from about 40°C to about 110°C. Preferable temperatures will be especially 60 – 90 °C.

Photo-initiators are usually required when the curing uses light, for example ultraviolet ("UV") light.

Preferred photo-initiators for use in free radical UV cure include, but are not limited to Radical Type I and/or type II photo-initiators.

Examples of radical type I photo-initiators are as described in WO 2007/018425, page 14, line 23 to page 15, line 26, which are incorporated herein by reference thereto.

Examples of radical type II photo-initiators are as described in WO 2007/018425, page 15, line 27 to page 16, line 27, which are incorporated herein by reference thereto. In case radical type II photo-initiators are used, preferably a synergist is also added. Preferred examples of synergists include, but are not limited to triethylamine, triethanolamine, methyl diethanolamine, ethyl 4-(dimethylamino)benzoate, 2-butoxyethyl 4-(dimethylamino)benzoate, 2-prop-2-enoyloxyethyl 4-(dimethylamino)benzoate and 2-ethylhexyl 4-(dimethylamino)benzoate.

A single type of initiator may be used but also a combination of several different types.

Preferably the composition used to form the curable copolymer comprises 0 to 8 wt%, more preferably 0.0001 to 8wt%, especially 0.001 to 5wt% and more especially 0.005 to 3wt% of initiator.

In view of the foregoing, curable copolymer is preferably obtainable by curing a composition comprising:

(i) 0.5 to 15wt% of an ethylenically unsaturated monomer comprising g an epoxide group (epoxide monomer);

(ii) 10 to 80wt% of an ethylenically unsaturated monomer comprising a poly(ethylene oxide) group (PEG monomer);

(iii) 0 to 10wt% of one or more further monomers;

(iv) 10 to 89.4999 wt% of inert solvent; and
(v) 0.0001 to 8wt% of initiator.

Preferably the amount of (i) + (ii) + (iii) + (iv) + (v) adds up to 100%. This does not exclude the presence of other components other than (i), (ii), (iii), (iv) and (v) but it sets the total amount of these four components. In one embodiment the composition consists solely of components than (i), (ii), (iii), (iv) and (v).

One may influence the ratio of m:n in the curable copolymer by controlling the molar ratio of epoxide monomer (i) to PEG monomer (ii) used to form the curable copolymer. For example, by increasing the molar ratio of epoxide monomer (i) to PEG monomer (ii) one may increase the ratio of m to n in the resultant curable copolymer.

One may influence the absolute values of m and n in the curable copolymer by controlling the copolymerization time and temperature, e.g. increasing the copolymerization time will increase the values of m and n.

The value of q in the curable copolymer is inherited from the number of consecutive ethyleneoxide groups present in the PEG monomer (ii) used to make the curable copolymer. Thus if one prepares the curable copolymer from an ethylenically unsaturated monomer comprising a chain of 20 consecutive ethylene oxide groups then q in the resultant copolymer will also be 20.

The value of m and n may be calculated from, for example, the number average molecular weight (NAMW) of the curable copolymer. One may also use other techniques such as size exclusion chromatography and epoxide content.

The values of m, n (m+n) and q may also be calculated from the amounts and identity of the components used to form it. Where the amounts and identity of the components used to form the GSM are not known, for example where the GSM has been obtained from a supplier who refuses to provide this information, one may determine the identity and amounts of components from which the GSM was obtained by analysis of the GSM, e.g. using pyrolysis and gas chromatography. A more preferred technique to analyze the components of the GSM is to hydrolyze the discriminating layer and analyze the hydrolysis product by size-exclusion chromatography or mass spectrometry. This method may be used to determine, for example, the value of (m+n) and q. This technique is particularly useful for determining the identity and ratio of monomers used to form the GSM. A suitable pyrolysis and gas chromatography technique which may be used to determine the composition of the DL in a GSM is described in the paper by H. Matsubara and H. Ohtani entitled “Rapid and Sensitive Determination of the Conversion of UV-cured Acrylic Ester Resins by Pyrolysis-Gas Chromatography in the Presence of an Organic Alkali” in Analytical Sciences, 2007, 23(5), 513.

The epoxide content of the curable copolymer may be determined by wet chemical analysis, for example a wet chemical analysis method in which epoxide groups are reacted with HBr and the obtained result is a number of epoxide groups per unit weight of the curable copolymer.

The value of (m+n) may also be determined from the epoxide content of the curable copolymer and the NAMW by GPC analysis.

Preferably the GSM is substantially non-porous. In other words, the GSM comprises pores having an average size (i.e. average pore size) which does not exceed the kinetic diameter of the gas molecules which are desired to be retained by (i.e. not pass through) the GSM.

A suitable method to determine the average pore size of a GSM is to inspect the surface thereof (typically the discriminating layer) by scanning electron microscope (SEM) e.g. using a Jeol JSM-6335F Field Emission SEM, applying an accelerating voltage of 2kV, working distance 4mm, aperture 4, sample coated with Pt with a thickness of 1.5nm, magnification 100 000×, 3° tilted view.

Preferably the discriminating layer has an average pore size of below 10nm, more preferably below 5nm, especially below 2nm. The maximum preferred pore size depends on the application e.g. on the gases to be separated.

Another method to obtain an indication of the porosity of a GSM is to measure its permeance to a liquid, e.g. water. Preferably the permeance of the GSM of the present invention to liquids is very low, i.e. the average pore size of the GSM is such that its pure water permeance at 20°C is less than 6.10−8m3/m2•s•kPa, more preferably less than 3.10−8m2•s•kPa.

The primary purpose of the porous substrate is to provide the GSM with mechanical strength without materially reducing gas flux. This results in the possibility of using a very thin discriminating layer on top, which is not possible to achieve with a free-standing (not supported) discriminating layer. Furthermore, the use of a porous substrate prevents the need of using fillers or additives to increase the mechanical strength of the discriminating layer.

The porous substrate is typically open-pored (before it is converted into the GSM), relative to the discriminating layer. Typically the porous substrate is sufficiently porous to allow the composition from which the discriminating layer is derived to enter the pores and partially impregnate the porous substrate.

The porous substrate preferably comprises one, two or more sheet materials. For example, in a preferred embodiment the porous substrate comprises a non-woven backing sheet as porous support(e.g. to provide mechanical strength). In this embodiment, the discriminating layer is preferably in contact with the backing sheet and optionally adheres it to the non-woven backing sheet. Examples of suitable non-woven backing sheets which may be used as porous support (e.g. for providing

mechanical strength) include microporous organic and inorganic membranes, woven or non-woven fabric. The non-woven backing sheet may be constructed from any suitable material. Examples of such materials include polysulfones, polyethersulfones, polyimides, polyetherimides, polyamides, polyamideimides, polyacrylonitrile, polycarbonates, polyesters, polyacrylates, cellulose acetate, polyethylene, polypropylene, polyvinylidenefluoride, polytetrafluoroethylene, poly(4-methyl 1-pentene), polyacrylonitrile and especially polyesters. One may use a commercially available porous sheet material as the backing sheet, if desired. Alternatively one may prepare the porous sheet material using techniques generally known in the art for the preparation of microporous materials.

The porous substrate may be bonded to the discriminating layer by partial permeation and curing of the composition used to form the discriminating layer. Preferably the porous substrate comprises a coating of polyacrylonitrile (PAN), polysulphone (PSf), polyether ether ketone (PEEK) and/or polytetrafluoroethylene (PTFE).

Examples of suitable porous substrates which are particularly good at receiving the composition used to form the discriminating layer include PAN, PSf, and PTFE.

Optionally the porous substrate or a component thereof, especially the backing sheet, has been subjected to a corona discharge treatment, glow discharge treatment, flame treatment, ultraviolet light irradiation treatment or the like, e.g. for the purpose of improving its wettability and/or adhesiveness.

The porous substrate preferably comprises a porous coating layer which has pores that have an average diameter at the surface which is smaller than the average diameter half way through the porous sheet material. In this embodiment, the pores half way through the porous sheet material preferably have an average diameter of 0.001 to 10μm, more preferably 0.01 to 1μm, when measured half way through the porous sheet. Furthermore, the pores preferably have a smaller average diameter at the surface of the porous substrate, e.g. an average diameter of 0.001 to 0.1μm, preferably 0.005 to 0.05μm. The pore diameters may be determined by, for example, viewing the surface of the porous substrate before it is converted to the GSM by scanning electron microscopy ("SEM") and by cutting through the porous substrate and measuring the diameter of the pores half way through the porous substrate, again by SEM.

The porosity at the surface of the porous substrate may also be expressed as a % porosity, i.e.

$$\% \text{ porosity} = 100\% \times \frac{\text{area of the surface which is missing due to pores}}{\text{total surface area}}$$

The areas required for the above calculation may be determined by inspecting the surface of the porous substrate by SEM. Thus, in a preferred embodiment, the

porous substrate has a % porosity >1%, more preferably >3%, and especially >10%. In contrast, the porosity of the porous substrate comprising a gutter layer (e.g. PTMSP or PDMS) was <1%.

The porosity of the porous substrate may also be expressed as a CO_2 gas permeance (units are $m^3(STP)/m^2.s.kPa$). Preferably the porous substrate has a CO_2 gas permeance of 5 to 150 x 10^{-5} $m^3(STP)/m^2.s.kPa$, more preferably of 5 to 100 x 10^{-5} $m^3(STP)/m^2.s.kPa$, most preferably of 7 to 70 x 10^{-5} $m^3(STP)/m^2.s.kPa$.

In contrast, when the porous substrate comprised a gutter layer (e.g. PTMSP or PDMS) the CO2 gas permeance of the porous substrate was much lower, typically below 5 x 10^{-5} $m^3(STP)/m^2.s.kPa$

Alternatively the porosity of the porous substrate may be characterised by measuring the N_2 gas flow rate through the porous substrate. Gas flow rate can be determined by any suitable technique, for example using a Porolux™ 1000 device, available from Porometer.com. Typically the Porolux™ 1000 is set at the maximum pressure (about 34 bar) and one measures the flow rate (L/min) of N_2 gas through the porous substrate under test. The N_2 flow rate through the porous substrate at a pressure of about 34 bar for an effective sample area of 2.69cm^2 (effective diameter of 18.5mm) is preferably >1L/min, more preferably >5L/min, especially >10L/min, more especially >25L/min. The higher of these flow rates are preferred because this reduces the likelihood of the gas flux of the resultant membrane being reduced by the porous substrate.

In contrast, when the porous substrate comprised a gutter layer (e.g. PTMSP or PDMS) the N2 gas flow rate of the porous substrate was much lower, typically below 1L/min.

The GSMs of the present invention are very robust, have few surface defects and retain good selectivity for long periods of time. These properties are retained even when the GSMs are used to separate gases at very high pressure and temperature and when feed gas comprises H_2S. In addition, the bond between the discriminating layer and the porous substrate is very strong and the GSM has good scratch resistance. Thus the GSMs of the present invention do not need a protective layer (PL) on top of the discriminating layer, although a PL may be included if desired.

The thickness of the various layers (e.g. the porous substrate, the discriminating layer and the optional (though unnecessary) protective layer) may be determined by cutting through the membrane and examining its cross section by SEM. The part of the discriminating layer which is present within the pores of the porous substrate is not taken into account when defining the thickness of the discriminating layer.

Preferably the GSM of the present invention has an average dry thickness (including the porous substrate) in the range 0.05 to 10μm, more preferably 0.09 to 5μm and especially 0.1 to 3μm.

Preferably the GSM has a H_2S/CH_4 selectivity ($\alpha H_2S/CH_4$) ≧30. Preferably the selectivity is determined by a process comprising exposing the membrane to a $CO_2/CH_4/nC_4H_{10}/H_2S$ = 47/33/0.5/0.1 (amounts by volume) of H_2S and CH_4 respectively at a feed pressure of 3760 kPa at 30°C.

Preferably the GSM has a permeability to H_2S of at least 300 Barrer. Preferably the GSM has a permeability to CH_4 of at most 10 Barrer. The permeability may be measured by the method described below.

According to a second aspect of the present invention there is provide a process for preparing a GSM according to the first aspect of the present invention which comprises the steps of:

(i) applying the composition for preparing the discriminating layer as defined in the first aspect of the present invention to a porous substrate; and

(ii) curing the composition thereby forming the discriminating layer on the porous substrate.

In a preferred embodiment the composition used to prepare the discriminating layer is applied to the porous substrate by a coating process. Examples of coating processes include slot die coating, slide coating, air knife coating, roller coating, screen-printing, and dipping. Depending on the used technique and the desired end specifications, it might be necessary to remove excess composition from the porous substrate by, for example, roll-to-roll squeeze, roll-to-blade or blade-to-roll squeeze, blade-to-blade squeeze or removal using coating bars.

Advantageously the GSMs of the present invention avoid the need for a gutter layer between the discriminating layer the porous substrate. This leads to lower raw materials costs and a simpler, cheaper manufacturing process for the GSMs. The target value of H_2S permeance for the GSMs of the present invention is below 700 GPU. Thus the present invention enables the preparation of GSMs in which the discriminating layer is not in contact with a gutter layer, e.g. not in contact with any layer comprising $Si-CH_3$ groups. Gas-separation membranes free from $Si-CH_3$ groups and in fact free from organosilicon groups may be prepared by the present invention. Thus the process according to the second aspect of the present invention enables one to use a porous substrate which is free from gutter layers.

Preferably the composition used to prepare the discriminating layer is applied to the porous substrate in a roll-to-roll process having high tension forces at unrolling and/or rolling the porous substrate of at least 50N/m^2. In even more preferred process the tension forces of unrolling or rolling the porous substrate are at least 100N/m^2.

The composition used to form the discriminating layer is preferably radiation-curable. Preferably irradiation to cure the composition begins within 7 seconds, more preferably within 5 seconds, most preferably within 3 seconds, of the composition being applied to the porous substrate.

Suitable sources of radiation include mercury arc lamps, carbon arc lamps, low pressure mercury lamps, medium pressure mercury lamps, high pressure mercury lamps, swirl flow plasma arc lamps, metal halide lamps, xenon lamps, tungsten lamps, halogen lamps, lasers and ultraviolet light emitting diodes. Particularly preferred are UV emitting lamps of the medium or high pressure mercury vapour type. In addition, additives such as metal halides may be present to modify the emission spectrum of the lamp. In most cases lamps with emission maxima between 200 and 450nm are particularly suitable.

The energy output of the irradiation source is preferably from 20 to 1000W/cm, preferably from 40 to 500W/cm but may be higher or lower as long as the desired exposure dose can be realized.

Irradiation in order to cure the composition used to prepare the discriminating layer may be performed once or more than once.

In order to produce sufficiently flowable composition for use in a high speed coating machine, the composition used to form the discriminating layer preferably has a viscosity below 4000mPa·s when measured at 25°C, more preferably from 0.4 to 1000mPa·s when measured at 25°C. Most preferably the viscosity of the composition is from 0.4 to 500mPa.s when measured at 25°C. For coating methods such as slide bead coating the preferred viscosity is from 1 to 100mPa.s when measured at 25°C. The desired viscosity is preferably achieved by controlling the amount of inert solvent in the composition and/or by appropriate selection of the components of the composition and their amounts.

With suitable coating techniques, coating speeds of at least 5m/min, e.g. at least 10m/min or even higher, such as 15m/min, 20m/min, 25m/min or even up to 100m/min, can be reached. In a preferred embodiment the composition used to form the discriminating layer is applied to the porous substrate at a coating speed as described above.

While it is possible to prepare the GSMs of the present invention on a batch basis with a stationary porous substrate, it is much preferred to prepare them on a continuous basis using a moving porous substrate, e.g. the porous substrate may be in the form of a roll which is unwound continuously or the porous substrate may rest on a continuously driven belt. Using such techniques the composition used to form the discriminating layer can be applied on a continuous basis or it can be applied on a large batch basis. Removal of any inert solvent present in the composition used to form the discriminating layer can be accomplished at any stage after the composition has been applied to the porous substrate, e.g. by evaporation or drying.

Thus in a preferred process for making the GSMs of the present invention, the composition used to form the discriminating layer is applied continuously to a porous substrate by means of a manufacturing unit comprising one or more composition application stations, one or more curing stations and a GSM collecting station, wherein the manufacturing unit comprises a means for moving the porous substrate from the

first to the last station (e.g. a set of motor driven pass rollers guiding the substrate through the coating line). The manufacturing unit optionally comprises one composition application station which applies the composition, e.g. a slide bead coater. The unit optionally further comprises one or more drying stations or IR-heating stations, e.g. for drying the final GSM.

The GSM is preferably in tubular form or, more preferably, in sheet form. Tubular forms of GSMs are sometimes referred to as being of the hollow fibre type. GSMs in sheet form are suitable for use in, for example, spiral-wound, plate-and-frame and envelope cartridges.

While this specification emphasises the usefulness of the GSMs of the present invention for separating gases, especially polar and non-polar gases, it will be understood that the GSMs can also be used for other purposes, for example providing a reducing gas for the direct reduction of iron ore in the steel production industry, dehydration of organic solvents (e.g. ethanol dehydration), pervaporation, oxygen enrichment, solvent resistant nanofiltration and vapour separation.

The GSMs of the present invention are particularly suitable for separating a feed gas containing a target gas into a gas stream rich in the target gas and a gas stream depleted in the target gas. For example, a feed gas comprising polar and non-polar gases may be separated into a gas stream rich in polar gases and a gas stream depleted in polar gases. In many cases the GSMs have a high permeability to polar gases, e.g. CO_2, H_2S, NH_3, SO_x, and nitrogen oxides, especially NO_x, relative to non-polar gases, e.g. alkanes, H_2, N_2, and water vapour.

The target gas may be, for example, a gas which has value to the user of the GSM and which the user wishes to collect. Alternatively the target gas may be an undesirable gas, e.g. a pollutant or 'greenhouse gas', which the user wishes to separate from a gas stream in order to meet product specification or to protect the environment.

Preferably the GSM has a H_2S/CH_4 selectivity ($\alpha H_2S/CH_4$) $\geqq 30$. Preferably the selectivity is determined by a process comprising exposing the GSM to a $CO_2/CH_4/nC_4H_{10}/H_2S$ = 77/22/0.7/0.3 (amounts by volume) of H_2S and CH_4 respectively at a feed pressure of 6000kPa at 40°C.

Preferably the GSM has a permeability to H_2S of at least 300 Barrer. Preferably the GSM has a permeability to CH_4 of at most 10 Barrer.

The permeability may be measured by the method described below.

Preferably the GSM is gas permeable and liquid impermeable.

According to a third aspect of the present invention there is provided a process for separating a feed gas comprising polar and non-polar gases into a gas stream rich in polar gases and a gas stream depleted in polar gases comprising bringing the feed gas into contact with a GSM according to the first aspect of the present invention.

Thus the GSMs of the present invention may be used for the separation of gases and/or for the purification of a gas

According to a fourth aspect of the present invention there is provided a gas-separation module comprising a GSM according to the first aspect of the present invention.

In the modules of the fourth aspect of the present invention the GSM is preferably in the form of a flat sheet, a spiral-wound sheet or takes the form of a hollow-fibre membrane.

The invention will now be illustrated by the following non-limiting Examples in which all parts are by weight unless specified otherwise.

The following materials were used in the Examples (all without further purification):

The following materials were used to prepare the GSMs described below:

ACVA	is 4,4′-azobis(4-cyanovaleric acid) thermal initiator from Sigma-Aldrich.(this initiator can polymerise unsaturated monomers while NOT opening epoxide rings).
n-BA	is n-butyl acetate (an inert solvent from Sigma-Aldrich/Merck).
I0591	is 4-isopropyl-4'-methyldiphenyliodonium Tetrakis(pentafluorophenyl) borate (an ring-opening adjuvant from TCI Chemicals). (this initiator can polymerise unsaturated monomers and also open epoxide rings).
MeOH	is methanol (an inert solvent).
GMA	is glycidyl methacrylate (an epoxide monomer from Sigma-Aldrich).
M-PEG-A	is methoxy poly(ethylene glycol) acrylate containing 13 sequential ethylene glycol units (a PEG monomer from Shin Nakamura Chemicals).
CD9038	is ethoxylated bisphenol A diacrylate (a crosslinking agent from Sartomer).
BYK	is polyether modified acryl functional polydimethylsiloxane BYK UV-3530 (an surfactant from BYK Chemie GmbH).
PEGDA	is poly(ethylene glycol) diacrylate containing 12 sequential ethylene glycol units with NAMW of 600 Da (a crosslinking agent from Sigma-Aldrich)

PAN	is a polyacrylonitrile porous substrate (MN PAN an ultrafiltration membrane from MicrodynNadir) comprising a PET sheet backing material coated with PAN having a CO_2 permeance 11 x 10^{-5} m^3(STP)/m^2.s.kPa and a N_2 gas flow of 2 L/min.
PSf	is a polysulfone porous substrate (Toraysulfone an ultrafiltration substrate from Toray Chemical Korea Inc.) having a CO2 permeance 15 x 10^{-5} m^3(STP)/m^2.s.kPa and a N2 gas flow above 5 L/min.
PTFE	is a polytetrafluoroethylene porous substrate (ultrafiltration substrate from Berghof-Fluoroplastics) having a CO2 permeance above 20 x 10^{-5} m^3(STP)/m^2.s.kPa and a N2 gas flow above 10 L/min.
Non-porous PET	is a non-porous, polyethylene terephthalate film (from Agfa) of 100 µm thicknesss.
M-PEG-A4	is methoxy poly(ethylene glycol) acrylate containing 4 sequential ethylene glycol units (from Sigma-Aldrich).
M-PEG-A13	is methoxy poly(ethylene glycol) acrylate containing 13 sequential ethylene glycol units (AM130-G from Shin Nakamura)
M-PEG-All	is methoxy poly(ethylene glycol) allyl ether containing 23 sequential ethylene glycol units (from Sigma-Aldrich).
A-PEG-OPh	is acrylate poly(ethylene glycol) phenyl ether containing 4 sequential ethylene glycol units.
PTMSP	is poly(1-(trimethylsilyl)-1-propyne) SSP-070 from Gelest (this is used to form a gutter layer).
PDMS	is polydimethylsilane DBE-C25 from Gelest (this is used to form a gutter layer).

M-PEG-MA is methoxy poly(ethylene glycol) methacrylate containing 9 sequential ethylene glycol units, purchased from Sigma-Aldrich.

Cyclohexanone was purchased from Sigma-Aldrich.

The performance of the GSMs of the present invention and Comparative GSMs were evaluated in the following tests:

Gas Selectivity and Permeability

The gas selectivity and permeability of each of the GSMs under test were measured using a feed gas having the composition $CO_2/CH_4/nC_4H_{10}/H_2S$ in the ratio 47/33/0.5/0.1 (by volume). The feed gas was passed through each GSM under test at a temperature of 30°C and feed pressure of 3760kPa using a circular gas permeation cell having a measurement diameter of 1.5cm. The flow rate, pressure, and gas composition of each feed gas, permeate gas, and retentate gas was calculated according formulation described in "Calculation Methods for Multicomponent Gas Separation by Permeation" (Y. Shindo et al, Separation Science and Technology, Vol. 20, Iss. 5-6, 1985) with "countercurrent flow" mode.

Permeability

The permeability (Pi) shown in Table 1 was measured as follows:

The permeability (Pi) of CO_2, H_2S, CH_4 and nC_4H_{10} was determined using the following equation:

$$Pi = (\theta_{Perm} \cdot X_{Perm,i}) / (A \cdot (P_{Feed} \cdot X_{Feed,I} - P_{Perm} \cdot X_{Perm,i}))$$

For example:

$$P(H_2S) = (\theta_{Perm} \cdot X_{Perm,H2S}) / (A \cdot (P_{Feed} \cdot X_{Feed,H2S} - P_{Perm} \cdot X_{Perm,H2S}))$$

$$P(CH_4) = (\theta_{Perm} \cdot X_{Perm,CH4}) / (A \cdot (P_{Feed} \cdot X_{Feed,CH4} - P_{Perm} \cdot X_{Perm,CH4}))$$

$$\alpha (H_2S/CH_4) = P(H_2S)/P(CH_4)$$

wherein:

Pi = Permeability of the relevant gas (i.e. is CO_2, H_2S, CH_4 or nC_4H_{10}) ($m^3(STP) \cdot m/m^2 \cdot kPa \cdot s$);

θ_{Perm} = Permeate flow rate ($m^3(STP)/s$);

$X_{Perm,i}$ = Volume fraction of the relevant gas in the permeate gas;

A = Membrane area (m^2);

P_{Feed} = Feed gas pressure (kPa);

$X_{Feed,i}$ = Volume fraction of the relevant gas in the feed gas;

P_{Perm} = Permeate gas pressure (kPa); and

STP is standard temperature and pressure, which is defined here as 25.0°C and 1 atmosphere pressure (101.325kPa).

The Barrer (P) was then determined by 1 Barrer = $1\times10^{-10}cm^3(STP)\cdot cm/(s \cdot cm^2 \cdot cmHg)$.

Selectivity

The selectivity (Sel) shown in Table 1 was measured as follows:

The membrane patch selectivity (H_2S/CH_4 selectivity; $\alpha(H_2S/CH_4)$) of the membrane under test for the gas mixture described in Table 2 was calculated from respectively from $P_{(H2S)}$ and $P_{(CH4)}$ calculated as described in (A) above based on following equations:

$$H_2S/CH_4 \text{ selectivity} : \alpha(H_2S/CH_4)= P_{(H2S)}/P_{(CH4)}$$

The permeance (Q) shown in Table C was measured as follows:

The permeance (Qi) of CO_2, H_2S, CH_4 and nC_4H_{10} was determined using the following equation:

$$Qi = Pi \cdot L$$

Qi = Permeance of the relevant gas (i is CO_2, H_2S, CH_4 or nC_4H_{10}) ($m^3(STP)/m^2\cdot kPa\cdot s$);

L = Thickness of discriminating layer in membrane [µm]

The Barrer (Q) was then determined by 1 GPU = $1\times10^{-6}cm^3(STP)/(s \cdot cm^2 \cdot cmHg)$.

Test for Defects in the Discriminating Layer - The Dying test

Defects in the discriminating layer (DL) of the GSMs under test were identified as follows: 6 drops of a dye solution ((a 1wt% solution of 1,4-bis[(2-ethylhexyl)amino]-anthraquinone (solvent blue) in n-heptane) were applied to the DL at room temperature and left in contact with the DL for 30 seconds. Then the excess of dye solution was removed from the DL and the DL was washed with n-heptane. The DL was then examined visually with the naked eye. If blue spots were visible on the DL this indicated the presence of defects (e.g. pinholes) and the GSM was scored "not okay" (abbreviated to NOK). If no blue spots were visible this indicated the absence of defects and the GSM was scored "okay" (abbreviated to OK).

Scratch testing:

Scratch durability of the GSM's DL were tested using a continuous loading scratching intensity tester manufactured by Shinto Scientific Co., Ltd. (Heidon). The

scratching of the DL was carried out at a velocity of 10 mm/second using a sapphire needle with a diameter of 5 mm, and a constant weight of 50 gram. The extent to which the DL surface was damaged by the scratching was evaluated visually and the performance of the GSM was measured after the DL had been scratched 40 times. The permeance and selectivity of the GSMs was measured before and after 40 scratches. The impact of the scratch durability was deemed to be okay if the permeance and selectivity of the GSM's DL after the 40 scratches did not fall below 90% of the permeance and selectivity before the 40 scratches.

Adhesion test:

This test measured how well the DL adhered to the porous substrate.

Adhesive tape (Saint-Gobain CHR® M741 polyester film backing silicone adhesive pressure sensitive tape, 20 cm-long×1.5 cm-wide) was applied to the DL of the GSM under test and a 1Kg roller was applied thereto for 1 minute at room temperature and a relative humidity of 50%. The GSM was firmly fixed in place and 2.5cm of the tape was then peeled from the DL of the GSM and attached to a tensile testing machine (Zwick Z010) at an angle of 180°. 75 mm of the tape was then peeled off, still at an angle of 180, at a speed of 5 cm/min. The data from the first 2.5 cm were ignored to ensure the test results were comparable and stable and the average force for the remaining 5cm tape removal was calculated. The adhesive tape was inspected to check whether any layers had been removed from the GSM. The force was increased until an inspection of the tape revealed that at least some of the GSMs layers (e.g. the DL) had been removed and was stuck on the tape. The force required to remove at least some of the DL from the GSM was noted, up to a maximum tested peeling force of 2.5 N/1.5cm. If the DL or any other layers were removed from the GSM using a force below 2.5 N/1.5 cm the GSM was scored not okay (NOK). If a force of 2.5 N/1.5cm did not remove any layers from the GSM the GSM was scored okay (OK).

Determination of the value of (m+n) in The Curable copolymer

The value of (m+n) in the curable copolymer was determined as follows:

The GSM was placed in 2.0 M HCl solution (aq.) for 16 hours. The solution was analysed for its polyacrylic acid content (arising from hydrolysis of the DL) by Gel Permeation Chromatography (GPC, Waters) and Liquid Chromatography Mass Spectrometry (LC-MS, Waters). The presence of polyacrylic acid is determined from LC-MS analysis, and the Mw and NAMW were determined from GPC analysis, of which the value of (m+n) could be determined by dividing the obtained Mw by the molecular weight of acrylic acid (72.06 g/mol).

Polydispersity

The polydispersity (PD) of the DL and/or the curable copolymer was determined by measuring its Mw and NAMW by GPC and dividing the Mw by the NAMW. The GPC analysis was performed using THF as an eluent and M-PEG-A as a reference for the calibration and calculation of the weight-average molecular weight (Mw) and NAMW.

Examples

(a) Preparation of Curable Copolymers (PPCs)

Curable Copolymers PPC1 to PPC12 comprising m epoxide groups and n poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q$ and comparative curable copolymers PPCC1 to PPCC2 not comprising such groups were prepared as follows: the monomers and the inert solvents indicated in Table A1 below were mixed at room temperature while purging with nitrogen gas for 1 hour. The resultant mixture was warmed to 75°C and then the initiator indicated in Table A1 was added as a 1wt% solution in MeOH. The mixture was stirred at 75°C for 16 hours and then cooled down to room temperature to give the desired PPC. The value of (m+n), Mw, Mn, and PD for the resultant PPCs were measured using the methods described above and the results are shown in Table A2.

Table A1: Preparation of Curable Copolymers*

Composition	PEG Monomer (i)	Epoxide Monomer (ii)	Further Monomer (iii)	Initiator (v)	Inert solvent (iv)	Curable Copolymer
	[Wt% relative to all curable monomers] (Wt% relative to composition)			[ratio monomers: initiator] (Wt% Initiator relative to composition)	(Wt% Solvent relative to composition)	
1	M-PEG-A13 [89.5] (44.8)	GMA [10.5] (5.3)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC1
2	M-PEG-A13 [97.5] (48.7)	GMA [2.5] (1.2)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC2

3	M-PEG-A13 [75.0] (37.5)	GMA [25.0] (12.5)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC3
4	M-PEG-A4 [90.0] (45.0)	GA [10.0] (5.0)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC4
5	M-PEG-MA [90.0] (45.0)	GMA [10.0] (5.0)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC5
6	M-PEG-All [90.0] (45.0)	AGE [10.0] (5.0)	-	ACVA [1000] (0.03)	n-BA - (45)	PPC6
7	M-PEG-A13 [90.0] (45.0)	GMA [10.0] (5.0)	-	ACVA [500] (0.02)	n-BA - (45)	PPC7
8	M-PEG-A13 [90.0] (45.0)	GMA [10.0] (5.0)	-	ACVA [250] (0.01)	n-BA - (45)	PPC8
9	A-PEG-OPh [90.0] (45.0)	GMA [10.0] (5.0)	-	ACVA [1000] (0.03)	MEK - (45)	PPC9
10	M-PEG-A13 [70.0] (35.0)	GMA [20.0] (10.0)	HO-PEG-A [10.0] (5.0)	ACVA [1000] (0.03)	EtOAc - (45)	PPC10
11	M-PEG-A13 [87.5] (43.7)	GMA [7.5] (3.7)	GA [5.0] (2.5)	ACVA [1000] (0.03)	CPME - (45)	PPC11
12	M-PEG-A13 [89.5] (44.7)	GMA [9.5] (4.7)	PEGDA [1.0] (0.5)	ACVA [1000] (0.03)	2-MeTHF - (45)	PPC12

13 (Comparative)	M-PEG-A13 [90.0] (45.0)	GMA [10.0] (5.0)	-	ACVA [1000] (0.03)	n-BA - (45)	PPCC1 (Comparative)
14 (Comparative)	M-PEG-A13 [90.0] (44.7)	GMA [10.0] (5.0)	-	ACVA [100] (0.3)	n-BA - (45)	PPCC2 (Comparative)

* The sum of all wt% relative to the total composition + wt% of MeOH sum up to 100%

Table A2: Analysis Results

	Value of q	Value of (m+n)	Mw (kDa)	NAMW (kDa)	Polydispersity (PD)
PPC1	13	830	665	405	1.64
PPC2	13	785	629	308	2.04
PPC3	13	739	592	317	1.87
PPC4	4	922	360	273	1.32
PPC5	9	645	412	266	1.55
PPC6	23	457	555	295	1.88
PPC7	13	1064	852	424	2.01
PPC8	13	1217	975	480	2.03
PPC9	4	832	388	298	1.30
PPC10	13	875	701	345	2.03
PPC11	13	832	666	338	1.97
PPC12	13	822	658	331	1.99
PPCC1 (Comparative)	30	762	610	339	1.80
PPCC2 (Comparative)	13	137	110	73	1.50

Preparation of additional Comparative Curable Copolymers

Additional comparative curable copolymers were prepared as described in Table A3 below and their properties are shown in Table A4 below:

Table A3: Additional Curable Copolymers

Composition	Monomer (wt% relative to composition)	Initiator [ratio monomers: initiator] (Wt% Initiator relative to composition)	Inert solvent (Wt% Solvent relative to composition)	Surfactant (Wt% surfactant relative to composition)	Curable Copolymer
15 (Comparative)	CD9038 (10.0)	I0591 (0.2)	MEK (89.3)	BYK (0.5)	PPCC3 (Comparative)
16 (Comparative)	PEGDA (10.0)	I0591 (0.2)	MEK (89.3)	BYK (0.5)	PPCC4 (Comparative)

Table A4: Analysis Results

Curable Copolymer	q	(m+n)	Mw (kDa)	NAMW (kDa)	PD
PPCC3 (Comparative)	30	1	2	2	1.00
PPCC4 (Comparative)	13	1	1	1	1.00

(b) Preparation of Compositions comprising the Curable Copolymers

Each of the curable copolymers listed in Tables A1 and A3 above (PPC1 to PPC12 and comparative PPCC1 to PPCC4) independently was formulated into a composition comprising that curable polymer (10wt%), MEK (89.3wt%), BYK (0.5wt%) and I0591 (0.2wt%) and the resultant compositions were stirred for at least 15 minutes to obtain a homogeneous mixture. Thus compositions C1 to C12 contained curable copolymers PPC1 to PPC12 respectively and comparative compositions CC1 to CC4 contained comparative curable copolymers PPCC1 to PPCC4 respectively.

(c) Preparation of GSMs using Ex1-Ex15 and CEx1-CEx5

The GSMs were prepared by coating compositions C1 to C12 and comparative compositions CC1 to CC4 from step (b) above onto the porous substrates shown in Table C1 below and then curing the compositions. In these Examples and

Comparative Examples the porous substrate shown in Table C1 and the above compositions were cured to form a discriminating layer thereon. More specifically, the GSMs in Examples Ex1 to Ex15 and Comparative Membranes CEx1 to CEx5 were prepared by coating each of the compositions indicated in Table C1, continuously and at 20°C, onto the porous substrate indicated using just one slot of a slide bead coating machine. The resultant, coated porous substrates were cured by passing them under an irradiation source (a Light Hammer LH6 from Fusion UV Systems fitted with a H-bulb working at 100% intensity) and then to a drying zone at 60°C. The resultant dried, GSMs then travelled to the collecting station. The thickness of the discriminating layer in each GSM (as shown in Table C1) was determined by cutting through the GSM and measuring the thickness of the discriminating above the porous substrate using a scanning electron microscope (SEM).

(d) GSM prepared for CEx6 and CEx7

The PDMS or PTMSP was dissolved in cyclohexane to give a 0.5wt% solution. The solution was coated on top of the porous substrate to obtain a substrate with a gutter layer on top. The resulting gutter layer was dried at room temperature for overnight and further dried at 50 °C in a vacuum oven until constant weight (no residual solvent present).

The resultant substrate comprising a PDMS gutter layer had a CO_2 permeance of 0.1 x 10^{-5} m^3(STP)/m^2.s.kPa and an N_2 flow of 0.05 L/min.

The resultant substrate comprising a PTMSP gutter layer had a CO_2 permeance of 0.2 x 10^{-5} m^3(STP)/m^2.s.kPa and an N_2 flow of 0.05 L/min.

The GSMs were prepared by coating the compositions described in (b) above and curing the compositions, thereby forming the discriminating layer on top using the method described in (c) and (d) above.

Table C1:

Example	Composition comprising a curable copolymer (a)	Porous substrate	Gutter layer	Thickness of the resultant discriminating layer (µm)
Ex1	C1	PAN	-	0.4
Ex2	C2	PAN	-	0.5
Ex3	C3	PAN	-	0.8
Ex4	C4	PAN	-	0.4
Ex5	C5	PAN	-	0.6
Ex6	C6	PAN	-	0.8
Ex7	C7	PAN	-	0.5
Ex8	C8	PAN	-	0.3

Ex9	C9	PAN	-	0.6
Ex10	C10	PAN	-	0.6
Ex11	C11	PAN	-	0.9
Ex12	C12	PAN	-	1.0
Ex13	C1	PSf	-	0.4
Ex14	C1	PEEK	-	0.5
Ex15	C1	PTFE	-	0.7
CEx1 (Comparative)	CC1	PAN	-	0.4
CEx2 (Comparative)	CC2	PAN	-	0.0
CEx3 (Comparative)	CC3	PAN	-	0.0
CEx4 (Comparative)	CC4	PAN	-	0.0
CEx5 (Comparative)	C1	No (non-porous PET)	-	1.8
CEx6 (Comparative)	C1	PAN	PTMSP	0.2
CEx7 (Comparative)	C1	PAN	PDMS	0.6

Notes:

1. CEx1 to CEx4 are comparative examples because the curable copolymer used to form the discriminating layer did not comprise m epoxide groups and n poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q$ as hereinbefore defined.
2. CEx5 is a comparative because the GSM lacked a porous substrate. Instead the discriminating layer was formed on non-porous PET.
3. CEx6 and CEx7 are comparative because the discriminating layer resulting from C1 was not in contact with the porous substrate. Instead a gutter layer separated the resultant discriminating layer from the porous substrate.

(d) Testing of the GSMs

The GSMs obtained in step (c) above were tested using the methods described above to determine their H_2S permeance ($Q(H_2S)$) and their H_2S/CH_4 selectivity ($\alpha(H_2S/CH_4)$). The results are shown in Table D1 below. A H_2S permeance ($Q(H_2S)$) above 150 GPU was deemed to be good. A H_2S/CH_4 selectivity ($\alpha(H_2S/CH_4)$) from 30 was deemed to be good. The DL of the GSMS were inspected for defects using the dying test described above.

From Table D1 it can be seen that the membranes according to the present invention have good H_2S permeance (>150 GPU) and very good H_2S/CH_4 selectivity (≧30).

Table D1 – Results

Example	Performance		Analysis*			
	Q(H_2S) (GPU)	α(H_2S/CH_4)	Dying test for defects	Scratch resistance result [relative Q, %] (relative α, %)	Value of (m+n)	Adhesion Test Results
Ex1	617	46	No	OK [98] (98)	830	OK
Ex2	589	45	No	OK [95] (99)	785	OK
Ex3	517	49	No	OK [90] (95)	739	OK
Ex4	610	43	No	OK [97] (98)	922	OK
Ex5	358	55	No	OK [100] (90)	645	OK
Ex6	188	50	No	OK [100] (99)	457	OK
Ex7	588	44	No	OK [97] (96)	1064	OK
Ex8	698	32	No	OK [98] (100)	1217	OK
Ex9	370	52	No	OK [95] (95)	832	OK
Ex10	325	49	No	OK [93] (97)	875	OK
Ex11	201	58	No	OK [95] (98)	832	OK
Ex12	156	63	No	OK [95] (95)	822	OK
Ex13	608	40	No	OK [92] (92)	830	OK
Ex14	609	39	No	OK [99] (93)	830	OK
Ex15	289	55	No	OK [97] (98)	830	OK
CEx1	631	23	Yes	ND	ND	OK
CEx2	249	29	Yes	ND	ND	OK
CEx3	1201	1	Yes	ND	ND	OK
CEx4	1200	1	Yes	ND	ND	OK
CEx5	1201	1	Yes	ND	ND	OK
CEx6	850	28	No	NOK [45] (60)	830	NOK
CEx7	887	29	No	NOK [30] (55)	830	NOK

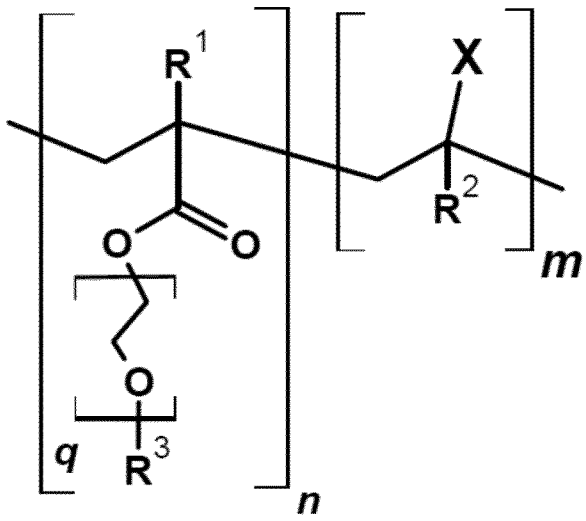
*ND = Not determined

CLAIMS

1. A gas-separation membrane comprising the following components:
(i) a porous substrate; and
(ii) a discriminating layer in contact with the porous substrate;
wherein the discriminating layer is obtainable by curing a composition comprising a curable copolymer, wherein the curable copolymer comprises m epoxide groups and n poly(ethylene oxide) groups of the formula $-(CH_2CH_2O)_q-$; wherein:

q has a value of 4 to 23; and
(m+n) has a value of 550 to 2,600.

2. The gas-separation membrane according to claim 1 wherein the curable copolymer comprises a group of Formula (1):



Formula (1)

wherein m, n, q and (m+n) are as defined above;
X is an epoxide-containing group;
each R^1 and R^2 independently is H or an optionally substituted alkyl group; and
R^3 is H or an optionally substituted alkyl or an optionally substituted phenyl group.
m has a value of 25 to 900;
n has a value of 400 to 1750;

3. The gas-separation membrane according to claim 1 or claim 2 wherein the GSM is free from gutter layers.

4. The gas-separation membrane according to any one of the preceding claims wherein the composition is substantially free from zeolites, porous silicas, carbon nanotubes, graphene oxides and/or metal-organic frameworks.

5. The gas-separation membrane according to claim 2 wherein each X independently further comprises at least one methylene group and optionally one or more groups selected from ester groups and ether groups.

6. The gas-separation membrane according to claim 2 or claim 5 wherein each X independently is an epoxide-containing group of the formula $-CH_2-O-CHCH_2O$ or $–CO_2-CH_2-CHCH_2O$.

7. The gas-separation membrane according to any one of the preceding claims wherein the copolymer of Formula (1) has a NAMW of 360 to 1500 kDa.

8. The gas-separation membrane according to any one of the preceding claims wherein:

m	has a value of 100 to 500; and/or
n	has a value of 500 to 1200; and/or
q	has a value of 6 to 20; and/or
(m+n)	has a value of 550 to 2600.

9. The gas-separation membrane according to any one of the preceding claims wherein the porous substrate comprises one or more porous supports.

10. The gas-separation membrane according to any one of the preceding claims wherein the porous substrate comprises a porous coating and a non-woven backing sheet.

11. The gas-separation membrane according to any one of the preceding claims wherein the discriminating layer is present within pores of the porous substrate and forms a layer on the porous substrate of average thickness 50 to 1,500 nm, when measured outwards from the surface of the porous substrate.

12. The gas-separation membrane according to any one of the preceding claims wherein the composition further comprises a crosslinking agent, an inert solvent, optionally a surfactant and optionally a radical initiator.

13. The gas-separation membrane according to any one of the preceding claims wherein the composition comprises:
    (a) 1 to 25wt% of the curable copolymer;
    (b1) 0 to 30wt% of a monomer having only one group reactive with the curable copolymer;
    (b2) 0 to 30wt% of crosslinking agent;
    (c) 40 to 99wt% of inert solvent;
    (d) 0.1 to 5wt% of surfactant; and
    (e) 0.005 to 8wt% of initiator.

14. The gas-separation membrane according to any one of the preceding claims wherein the curable copolymer is obtainable from a composition comprising:
    (i) 0.5 to 15wt% of an ethylenically unsaturated monomer comprising an epoxide group;
    (ii) 10 to 80wt% of an ethylenically unsaturated monomer comprising a poly(ethylene oxide) group;
    (iii) 0 to 10wt% of one or more further monomers;
    (iv) 10 to 89.4999 wt% of inert solvent; and
    (v) 0.0001 to 8wt% of initiator.

15. The gas-separation membrane according to claim 14 wherein the curable copolymer is obtained by thermal curing.

16. A process for preparing a gas-separation membrane according to any one of claims 1 to 14 which comprises the steps of:
    i. impregnating a porous substrate with a composition according to any one of claims 1 to 14; and
    ii. curing the composition.

17. The process according to claim 16 wherein the porous substrate is free from gutter layers.

18. A gas-separation module comprising a gas-separation membrane according to any one of claims 1 to 15.

19. The gas-separation module according claim 18 which further comprises a permeate spacer and feed spacer.

20. Use of a gas-separation membrane according to any one of claims 1 to 15 or a gas-separation module according claim 18 or 19 for separating gases and/or for purifying a feed gas.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/055522

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D71/40 B01D46/00 B01D53/22 B01D71/82 B01D69/12
B01D71/76 B01D71/52
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/251883 A1 (NIU Q JASON [US]) 1 November 2007 (2007-11-01)	1-19
A	paragraphs [0019], [0039] - [0043], [0056], [0058]; claim 4; tables 1,2,4	20

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[x] Further documents are listed in the continuation of Box C.
[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search	Date of mailing of the international search report
20 May 2022	31/05/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Williams, Jennifer

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MA LIANG ET AL: "Mixed Matrix Membrane Based on Cross-Linked Poly[(ethylene glycol) methacrylate] and Metal-Organic Framework for Efficient Separation of Carbon Dioxide and Methane", ACS APPLIED NANO MATERIALS , vol. 1, no. 6 22 June 2018 (2018-06-22), pages 2808-2818, XP055850976, ISSN: 2574-0970, DOI: 10.1021/acsanm.8b00459 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acsanm.8b00459 [retrieved on 2021-10-13] Sections 2.1, 2.7, 2.9, 3.2; table 1 abstract -----	1-20
X	KR 102 225 357 B1 (UNIV YONSEI IACF [KR]) 9 March 2021 (2021-03-09) paragraphs [0012] - [0014], [0027] - [0035], [0048], [0054], [0055]; figures 1a,6,8,9a,9b,10c; table 2 -----	1,2,4,6, 8-16,18, 20

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Information on patent family members

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