

ULTRA-PERMEABLE MEMBRANES FOR GAS SEPARATION

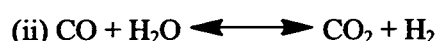
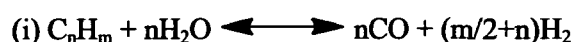
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BACKGROUND OF THE INVENTION

Industrial emissions produce green house gases that have a negative impact on the environment. It is desirable to control them by separating the harmful green house gases from the others.

Another means to minimize green house gas levels is to use energy sources other than fossil fuels, e.g., hydrogen gas. Such gases also require separation. For example, most industrial production of hydrogen is based on a two-step process:

15



It is essential to separate the carbon dioxide from the hydrogen thus produced.

Membranes have been used to separate gases. For industrial use, they need to be selective and permeable while maintaining durability. There is a need to develop durable membranes that have both high permeability and sufficient selectivity for separating gases.

SUMMARY OF THE INVENTION

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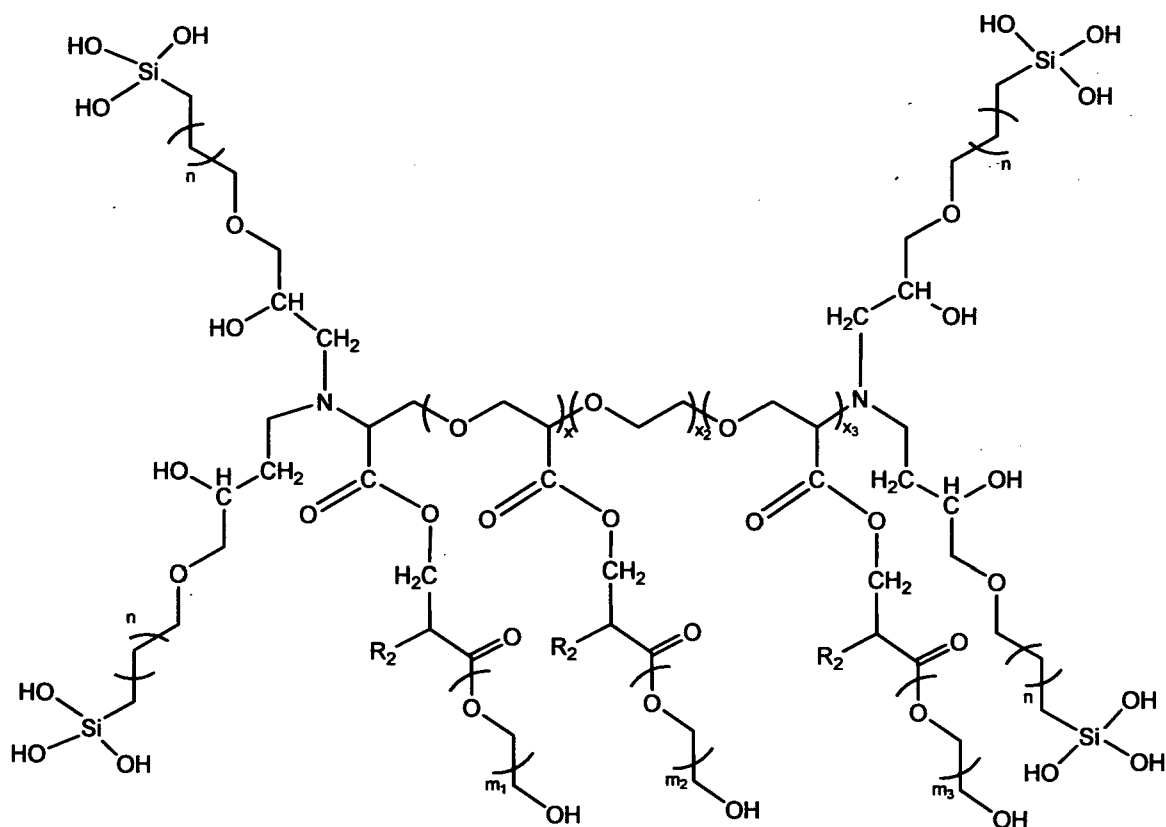
One aspect of this invention relates to a monomer containing (i) a poly(alkylene) oxide backbone having 20 to 1000 (e.g., 20 to 400 or 20 to 100) carbon atoms and 10 to 500 (e.g., 10 to 200 or 10 to 50) oxygen atoms with a carbon/oxygen ratio being 1:1 to 10:1 (e.g., 2:1 and 3:1); (ii) 1 to 100 (e.g., 1 to 40) poly(alkylene) oxide side chains attached to the backbone, wherein each chain has 10 to 500 (e.g., 10 to 200 or 10 to 100) carbon atoms and 5 to 250 (e.g., 5 to 100 or 5 to 50) oxygen atoms with a carbon/oxygen ratio being 1:1 to 10:1 (e.g., 2:1 and 3:1); and (iii) one to eight cross-linking groups (e.g., four) also attached to the backbone, each cross linking group having two to four binding moieties (e.g., three). The side chains are of a shorter length than the backbone. This

monomer is capable of cross linking other monomers having the same structural features to form a polymer via its binding moieties and the binding moieties of the other monomers. An example of a cross linking group is $-\text{Si}(\text{OH})_3$, which has three binding moieties (e.g., three OHs).

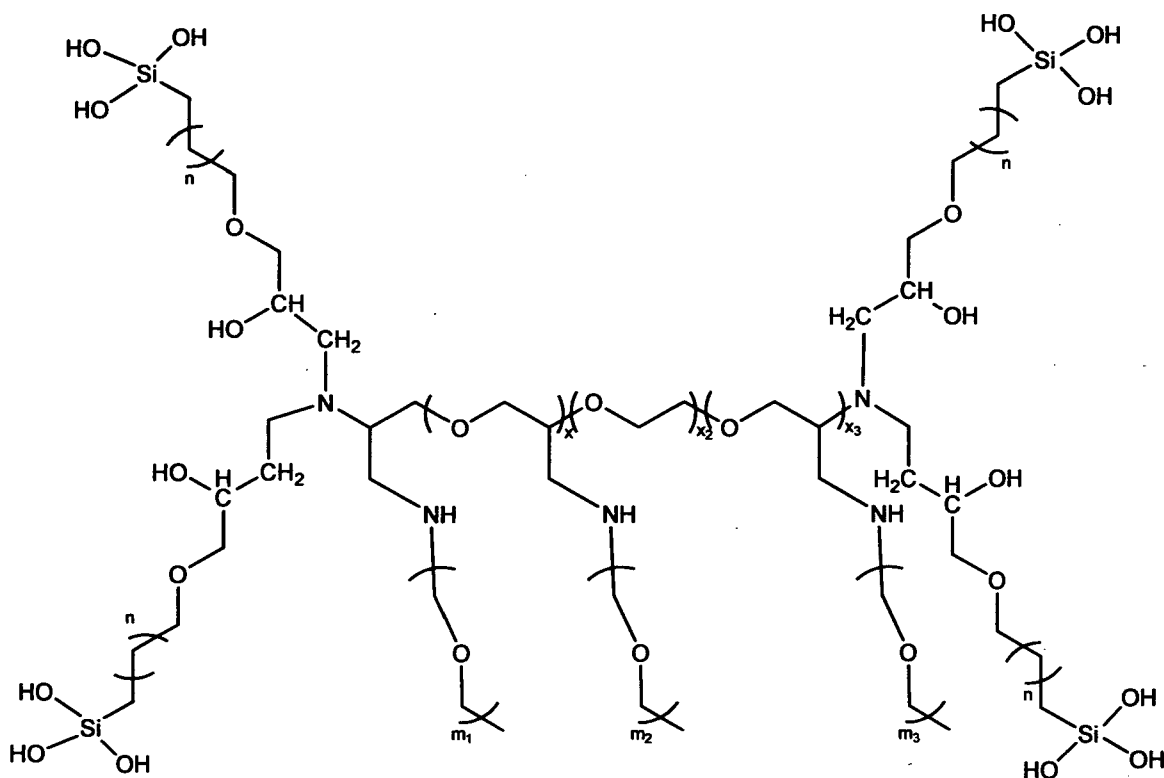
5 The term “poly(alkylene) oxide” refers to a chain of repeating alkylene oxides, e.g., poly(ethylene oxide), poly(propylene oxide), and poly(butylene oxide.) The term “alkylene oxide” refers to an ether-containing hydrocarbon, having 1-10 carbon atoms, e.g., ethylene oxide, propylene oxide, and butylene oxide.

In one embodiment of this monomer, one to three cross-linking groups attach to
10 each end of the backbone.

Below are two exemplary monomers of this invention:



and



Another aspect of this invention is a polymer that includes a plurality of the above described monomers cross linked to each other.

- 3 -

A still further aspect of this invention relates to another method of preparing a branched cross linker-containing poly(alkylene) oxide chain. The method includes reacting a poly(alkylene) oxide backbone, having a first reactive group and a second reactive group, with two to eight cross linkers, each having a third reactive. The third reactive group of a cross linker covalently bonds with the first reactive group and the third reactive group of another cross linker covalently bonds with the second reactive group to form a cross linker-containing poly(alkylene) oxide backbone. Each of the cross linkers used in this method has two to four binding moieties. This method also includes generating free radicals on the cross linker-containing poly(alkylene) oxide backbone and reacting poly(alkylene) oxide side chains, each having a fourth reactive group at one end, with the cross linker-containing poly(alkylene) oxide backbone to form a branched cross linker-containing poly(alkylene) oxide chain, via covalent bonding of the fourth reactive group or groups to the cross linker-containing poly(alkylene) oxide backbone. In other words, the side chains form branches off the backbone by covalently bonding to the backbone.

A still further aspect of this invention relates to a method of reacting a plurality of branched cross linker-containing poly(alkylene) oxide chains to form a polymer via bonding between binding moieties in one chain to binding moieties in other chains.

Yet another aspect of this invention is a method of altering the composition of a gaseous mixture. This method includes providing a membrane formed of a polymer of this invention and passing a gaseous mixture through the membrane. The gaseous mixture having a first gas (e.g., H₂, N₂, CH₄, O₂, and C₃H₈) and a second gas (e.g., CO₂, H₂S, CO, and H₂O). In one embodiment, the first gas is H₂ and the second gas is CO₂. Two methods of preparing the membrane are described below.

Also within the scope of this invention is a method of preparing a membrane. The method includes first preparing a solution containing poly(alkylene) oxide backbones, poly(alkylene) oxide chains, and a solvent, the backbones and the chains being dispersed in the solvent; and then providing a layer of the solution. Each of the backbones has two to eight cross linking groups and each of the cross linking groups has two to four binding moieties. Subsequent steps of this method include cross linking the backbones via

covalent bonding between binding moieties in one backbone to binding moieties in other backbones, and finally removing the solvent to form a membrane. In the membrane thus formed, the chains are blended with the cross linked backbones. In other words, the chains are non-covalently embedded within the cross linked backbones.

5 Further within the scope of this invention is another method of preparing a membrane. The method includes first preparing a solution containing poly(alkylene) oxide backbones, poly(alkylene) oxide chains, and a solvent, the backbones and the side chains being dispersed in the solvent; and then providing a layer of the solution. Each of the backbones has two to eight cross linking groups, each of cross linking groups has two
10 to four binding moieties, and each of the chains has a reactive group at an end. Subsequent steps of this method include cross linking the backbones via covalent bonding between binding moieties in one backbone to binding moieties in other backbones, then removing the solvent to obtain the membrane, and finally generating free radicals on the poly(alkylene) oxide backbones. The chains, via the reactive groups, are
15 covalently bonded to, not blended with, the backbones.

The membranes prepared by the above described methods are also within the scope of this invention.

The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be
20 apparent from the detailed description of several embodiments and also from the appending claims.

DETAILED DESCRIPTION OF THE INVENTION

This invention is based in part on an unexpected discovery that certain polymers
25 composed of monomeric cross linker-containing poly(alkylene) oxides or blends thereof have increased permeability for H₂ and CO₂ and selectivity for the gas pair CO₂/H₂.

Described below, for illustrative purposes, is a modification to a previous approach of fabricating membranes containing a cross-linked network of PEO/silica. See Shao et al., *International Journal of Hydrogen Energy* 2009; 34:6492-6504. As a result
30 of this modification, CO₂ permeability is increased to 942 Barrer and H₂ permeability to

103 Barrer. This modification enables the grafting of short poly(ethylene glycol) chains onto the backbone of the PEO/silica polymer to form a branched polymer, which results in the increments in H₂ and CO₂ permeability whilst slightly enhancing the H₂/CO₂ selectivity. This modified approach can be extended to other types of PEO/silica

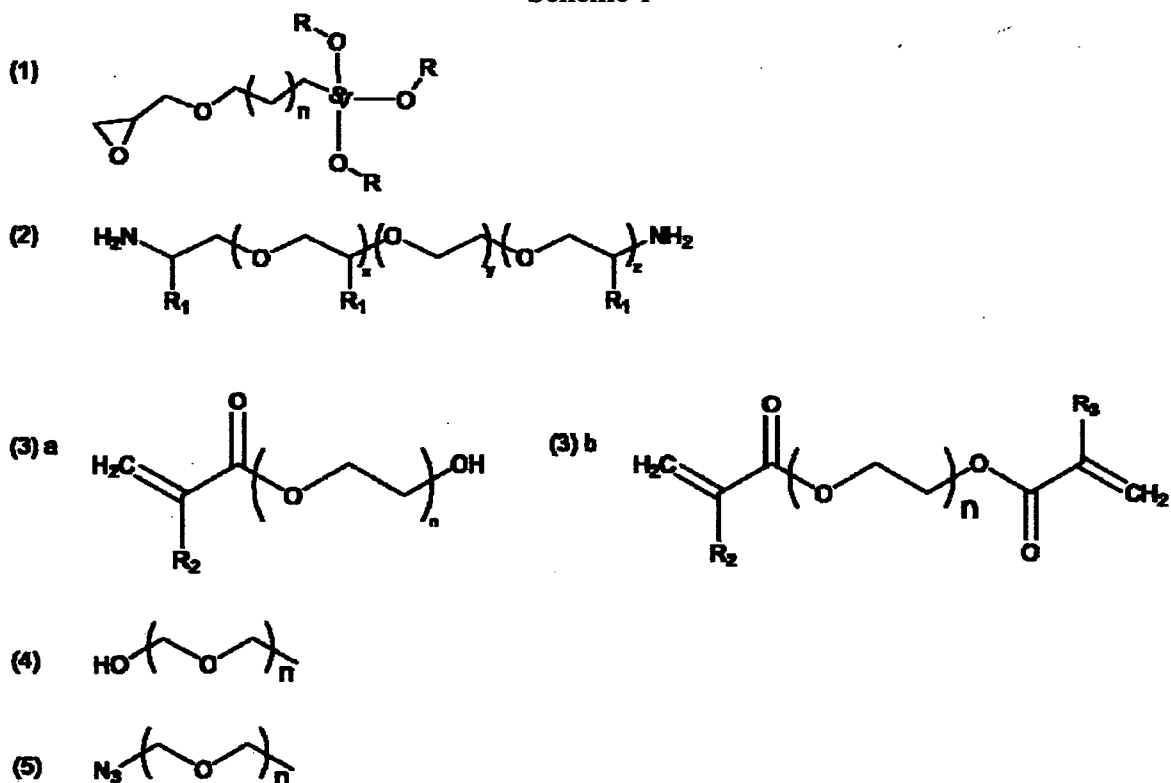
5 polymers.

Without further elaboration, it is believed that one skilled in the art can, based on the disclosure herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely descriptive, and not limitative of the remainder of the disclosure in any way whatsoever. All publications

10 cited herein are incorporated by reference.

Scheme 1 shows the compounds with the following structural formula that were used for the fabrication of PEO/silica membranes and were subsequently modified to obtain membranes that display ultrahigh permeability:

Scheme 1



(1) The first compound used is primarily made up of an organic epoxy moiety and an $\text{Si}(\text{OR})_3$ moiety. R denotes an alkyl organic group.

5 (2) The second compound used is made up of organic ethylene oxide moieties couple with amine groups at both ends chain. The length of the chain depends on the repeating units of the ethylene oxide groups. R1 can be H, a CH_3 group or a COOH group.

(3) The third compound used is made up of at least one methacrylate groups at the end of a chain of ethylene oxide groups. R2 and R3 could be made up of CH_3 or H groups.

(4) The fourth compound used is made up of a chain of ethylene oxide units and a hydroxide unit.

10 (5) The fifth compound used is made up of a chain of ethylene oxide units and an azide unit.

Example 1. Preparation of PEO-silica solution

15 A pre-determined amount of PEG-diamines was dissolved in a mixture solution containing 70 wt% deionized water and 30 wt % ethanol. The inorganic epoxy containing silane ca. (1 mole) was hydrolyzed using a mixture solution that contains 1.13 moles of ethanol, 3.2 moles of deionized water, and 0.05 moles of hydrochloric acid (37.5%). The hydrochloric acid acts as a catalyst in this hydrolysis reaction. After 30 minutes of
20 hydrolysis at room temperature, the alkoxysilane solution was immediately mixed with the PEG-diamine solution. The epoxy-amine reaction was facilitated by vigorous stirring for 1 hour at 60°C.

Example 2. Fabrication of PEO-silica polymer with PEGMA grafts/cross-links

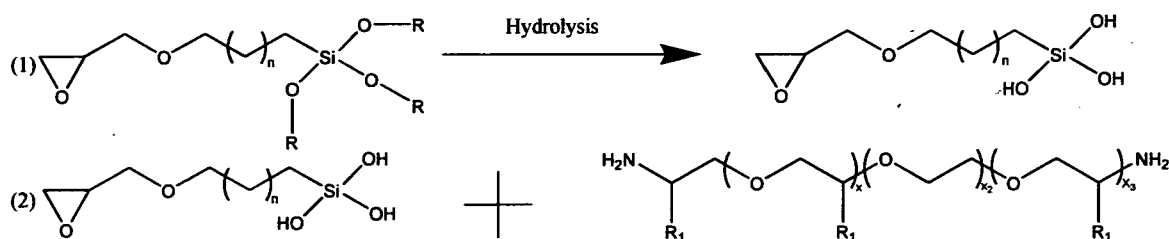
25 Subsequently, the PEO-silica solution from Example 1 was exposed to wet ozonolysis treatment for 30 seconds. The flow rate of the ozone gas was set to 0.5 LPM. The purpose of wet ozonolysis was to generate free radicals on the backbone chains so that free radical polymerization could take place when short poly (ethylene glycol) chains (PEG) coupled with one or two methyl methacrylate groups (PEGMA) were added to the
30 radicalized polymeric solution. 20-75 wt% of the short chain PEG were added to the ozonolyzed polymeric solution. To ensure that PEGMA react with the radicalized backbones, the mixture of solution was stirred for at least 3 hours.

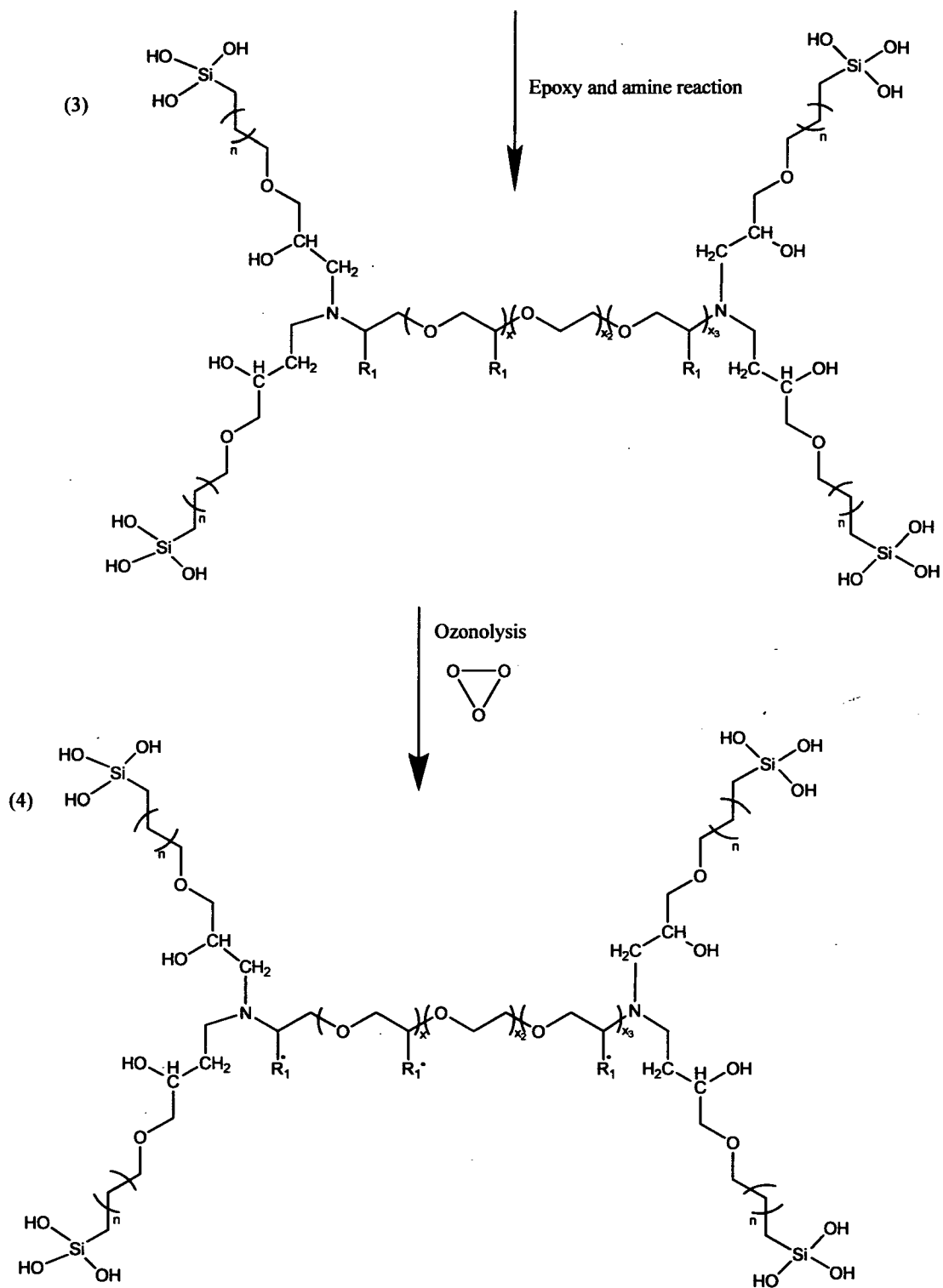
The above-mentioned mixture was ultrasonicated in a water bath for 10 minutes at room temperature to remove trapped air. Subsequently, the solution was cast slowly on to
35 a Teflon dish and the solvent was evaporated at 30°C for 1 day, and 40°C for at least 2

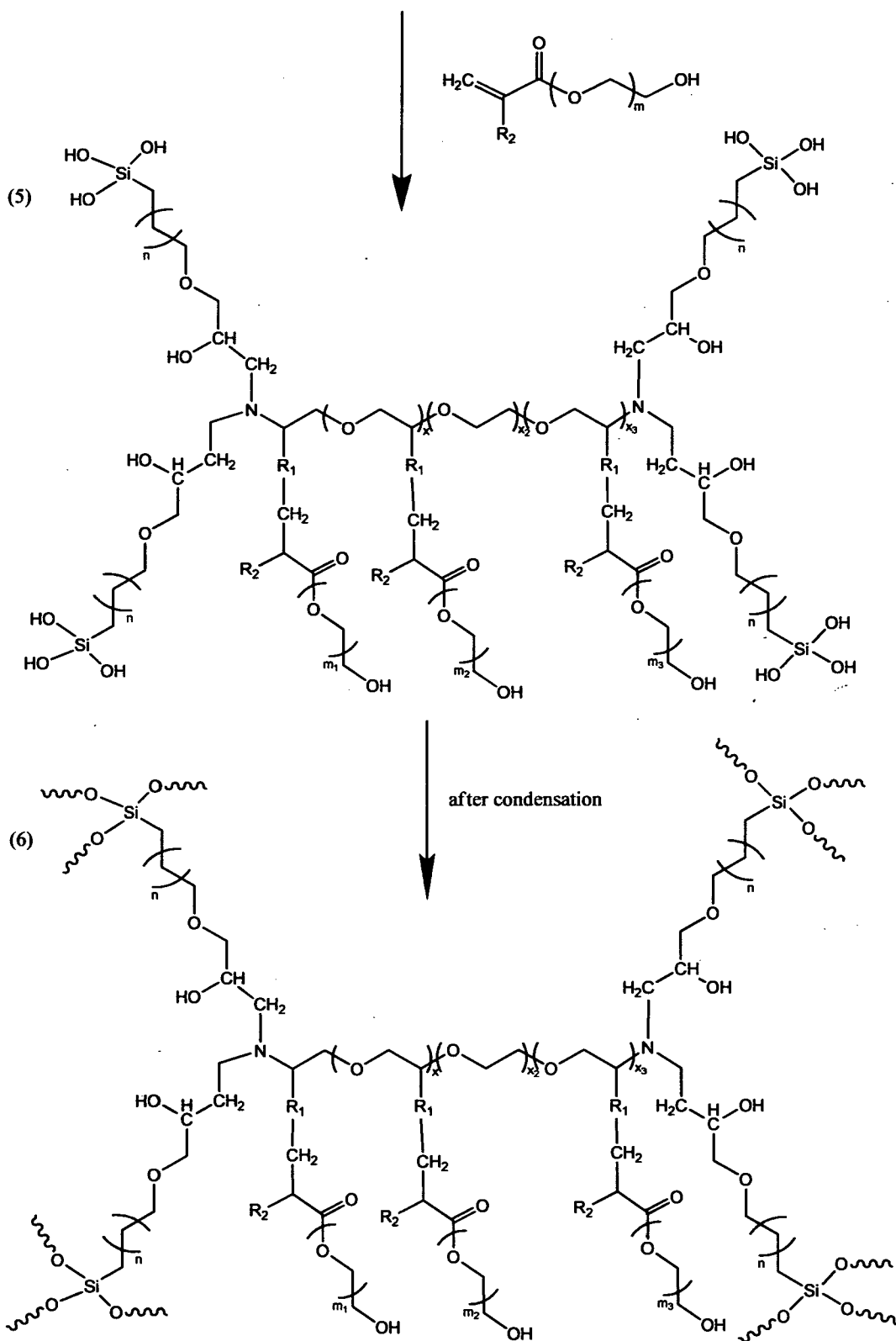
days. Thereafter, the nascent films were dried in a vacuum oven at 70°C for 24 hours to eliminate residual solvent and unreacted PEGMA. This process also promotes further reacting between the organic and inorganic components as well as facilitating condensation. After the drying process, the dried films were removed from the Teflon dish and kept in a dry environment.

The structural and performance changes in the PEO/silica polymer could be ascribed to free radical formation during the wet ozonolysis process that reacted with the methacrylate groups of the PEGMA. From the reaction mechanism shown in Scheme 2, it is evident that the reaction took place between the methacrylate groups of PEGMA and the radicalized pendent R1 groups (e.g., $\text{CH}_2^\bullet$ or $\text{COO}^\bullet$) in the PEO main chain.

Scheme 2







The ratio of PEGMA to PEO/silica varied from 0 wt% to 60 wt% with respect to the PEO/silica polymer. The ratios of PEO to silica used were 50:50 wt%; 75:25 wt%; and 80:20 wt%. When the amount of ethylene oxide units in the membrane increased, the H₂ and CO₂ permeability of the PEO/silica polymer increased. The increment of H₂ permeability of PEGMA modified PEO/silica polymer increased slightly when the PEGMA increased from 20 wt% to 60 wt%, as seen in Table 1. Compared to the increment in CO₂ permeability when PEGMA content increased from 20 to 60-wt%, the increments in H₂ permeability appeared to be much smaller.

Table 1

CO₂/H₂ separation capabilities of PEO-GOTMS/PEGMA membranes at 35°C

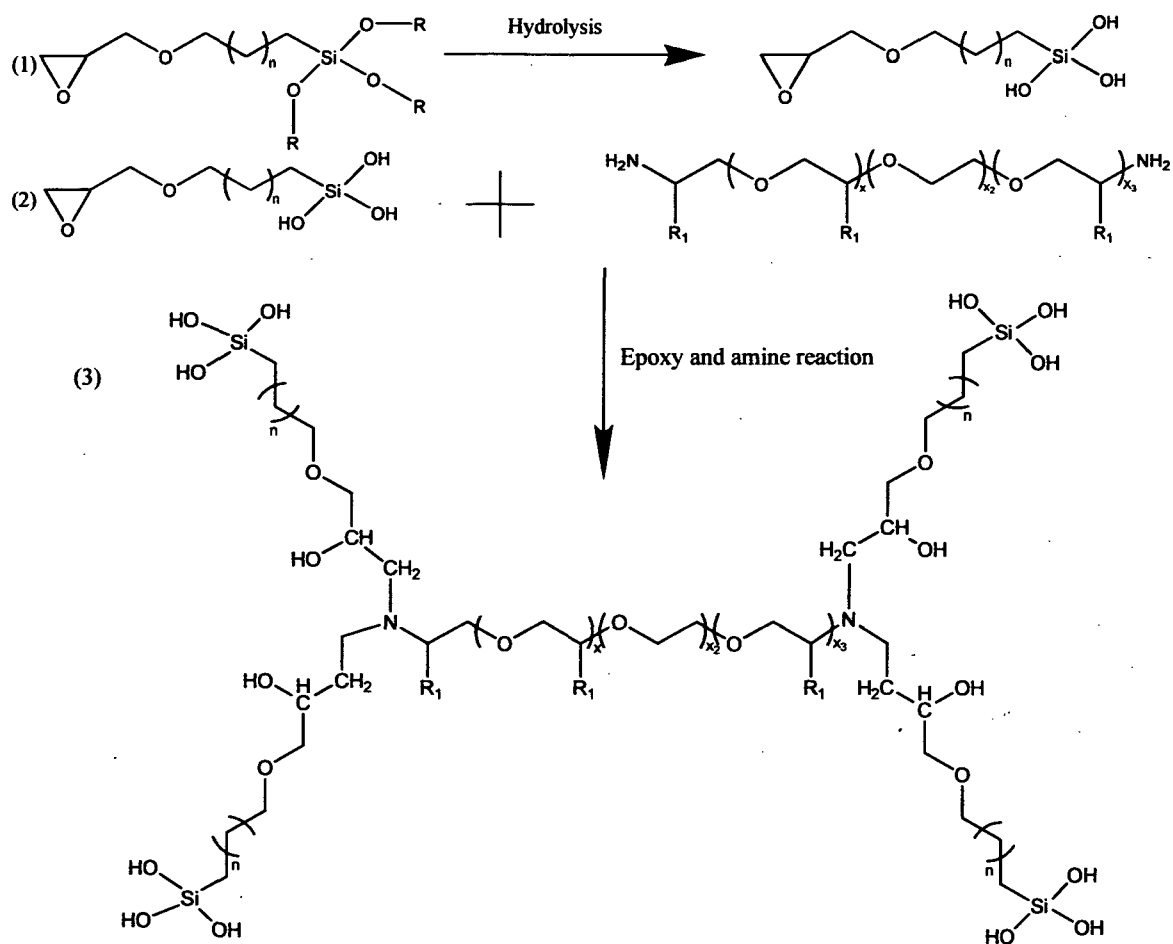
Sample Name	PEO (wt%)	GOTMS (wt%)	PEGMA: PEO-GOTMS (wt%)	H ₂ (barrer)	CO ₂ (barrer)	α CO ₂ /H ₂
PEO(50)-GOTMS(50)	50	50	0	25.5	193	7.57
PEO(50)-GOTMS(50):PEGMA(11)	50	50	11	95	678	7.12
PEO(50)-GOTMS(50):PEGMA(27)	50	50	27	101	829	8.20
PEO(50)-GOTMS(50):PEGMA(33)	50	50	33	103	943	9.13
PEO(50)-GOTMS(50):PEGMA(43)	50	50	43	122	1056	8.64
PEO(75)-GOTMS(25)	75	25	0	27	241	8.94
PEO(75)-GOTMS(25):PEGMA(11)	75	25	11	108	994	9.2
PEO(75)-GOTMS(25):PEGMA(27)	75	25	27	116	1101	9.5
PEO(75)-GOTMS(25):PEGMA(33)	75	25	33	156	1601	10.26
PEO(75)-GOTMS(25):PEGMA(43)	75	25	43	166	1805	10.86
PEO(80)-GOTMS(20)	30	70	0	39	377.65	9.68
PEO(80)-GOTMS(20):PEGMA(11)	30	70	11	110	1078	9.78
PEO(80)-GOTMS(20):PEGMA(27)	30	70	27	134	1323	9.86
PEO(80)-GOTMS(20):PEGMA(33)	30	70	33	155	1546	9.97
PEO(80)-GOTMS(20):PEGMA(43)	30	70	43	195	1988	10.21

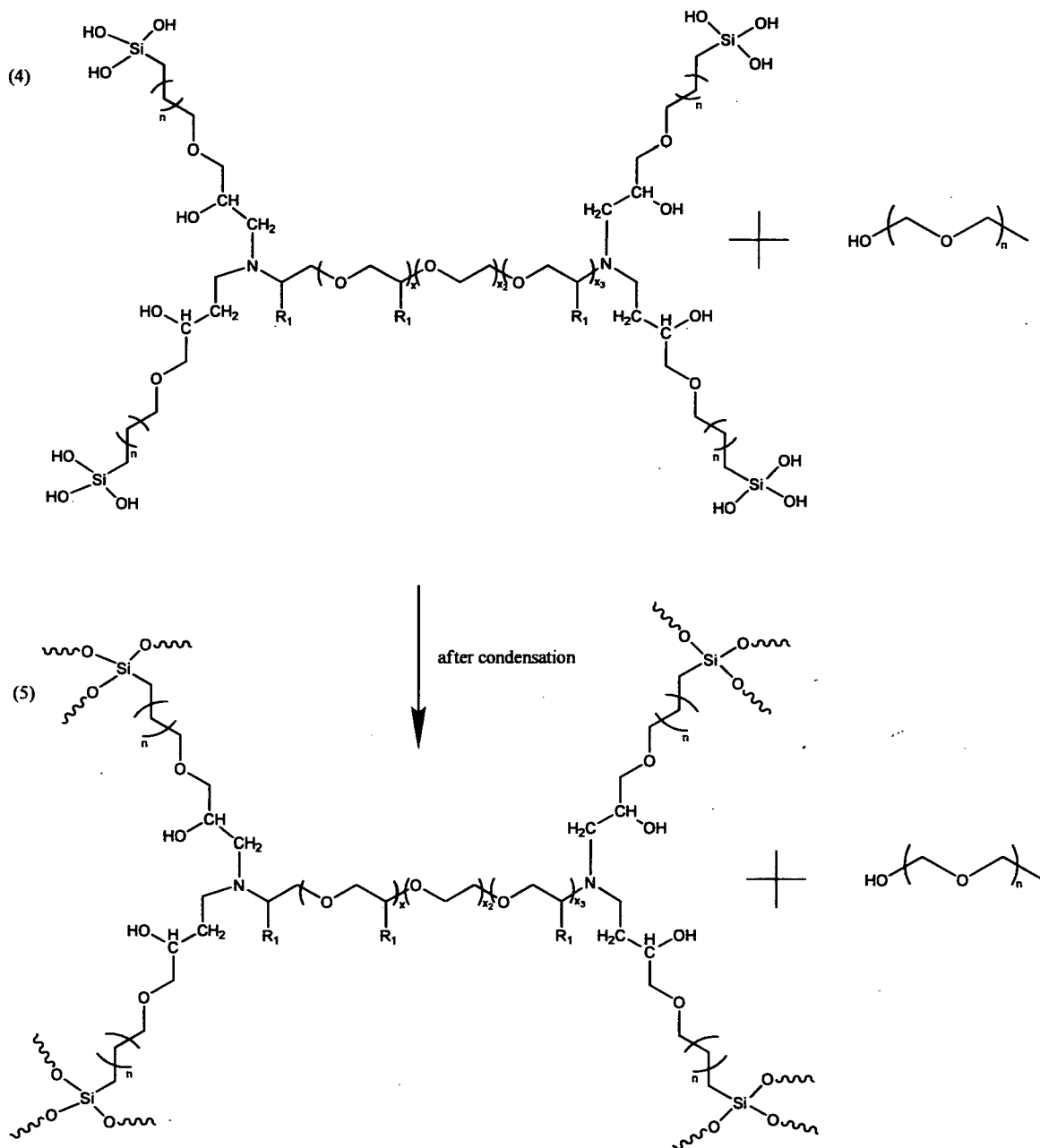
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Example 3. Physical blending of PEO-OH and PEO-silica polymers

In this fabrication process, pre-determined amounts of PEO-OH were added to the PEO-silica solution produced using the above-mentioned procedure in Example 1. This mixture was ultrasonicated in a water bath for 10 minutes at room temperature to remove trapped air. Subsequently, the solution was cast slowly on to a Teflon dish and the solvent was evaporated at 30°C for 1 day, and 40°C for at least 2 days. Thereafter, the nascent films were dried in a vacuum oven at 70°C for 24 hours to eliminate residual solvent. This process also promotes further reacting between the organic and inorganic components as well as facilitating condensation. After the drying process, the dried films were removed from the Teflon dish and kept in a dry environment. Scheme 3 depicts possible chemical reactions.

Scheme 3





- 5 The ratio of mPEO-OH to PEO/silica varied with respect to the PEO/silica polymer. From Table 2, increments in H_2 , N_2 , and CO_2 permeability were observed when the amount of ethylene oxide units increased. All tested gas permeabilities increased as a function of temperature. With increased temperatures, polymer chain rigidity is reduced. Hence, gas permeability will increase. It is also evident that CO_2/H_2 and CO_2/N_2 gas

selectivities decreased as a result of increased mPEO-OH molecular weight. High gas permeabilities are also attained in less-desired physical blends.

Table 2
CO₂/H₂ and CO₂/N₂ separation capabilities of
PEO-GOTMS/mPEO-OH physical blend
membranes at different temperatures

Sample Name	Temperature (°C)	H ₂ permeability (Barrer)	N ₂ permeability (Barrer)	CO ₂ permeability (Barrer)	CO ₂ /H ₂ selectivity	CO ₂ /N ₂ selectivity
GPP312 1k	35	62.8	11.0	497	7.9	45.2
	40	226.4	31.6	2200	9.7	69.6
	45	271.7	39.7	2436	9.0	61.4
GPP814 2k	35	16.4	3.01	55.0	3.4	18.3
	50	50.6	10.6	154	3.0	14.5
	60	202.9	154.1	1413	7.0	9.2

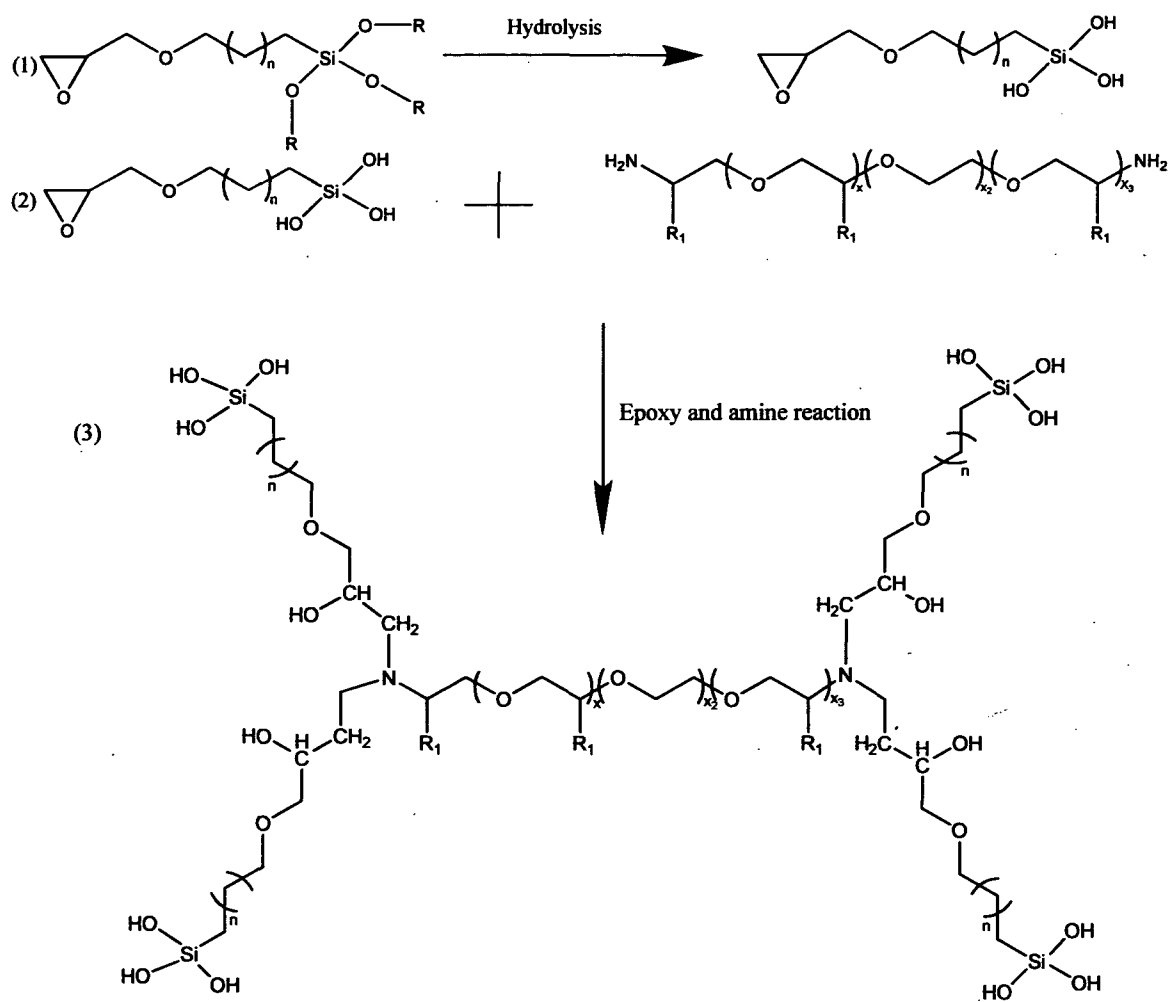
GPP814 2k: GOTMS:PEO:mPEO-OH molar ratio = 8:1:4 mPEO-OH Mw=2k

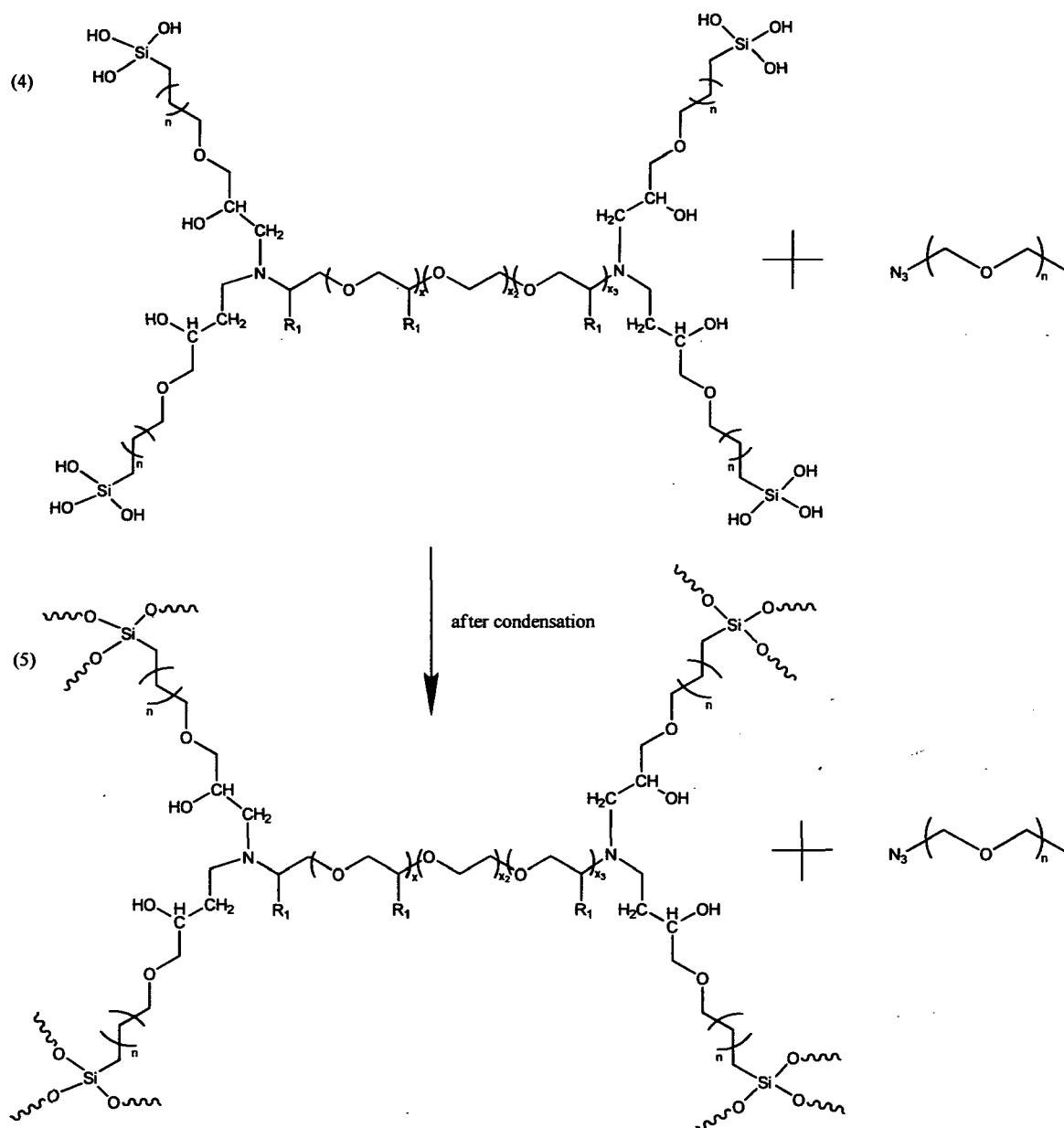
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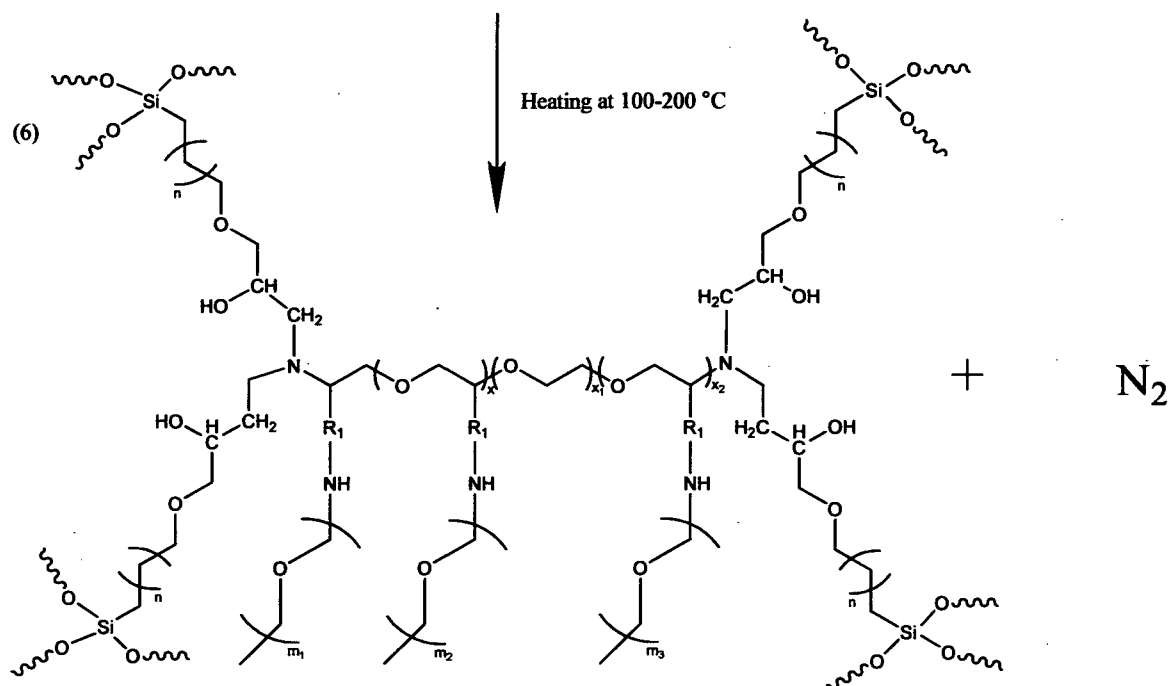
Example 4. Reacting of PEO-azide with PEO-silica polymers

Pre-determined amounts of PEO-azide were added to the PEO-silica solution produced using the above-mentioned procedure in Example 1. The above-mentioned mixture was ultrasonicated in a water bath for 10 minutes at room temperature to remove trapped air. Subsequently, the solution was cast slowly on to a Teflon dish and the solvent was evaporated at 30°C for 1 day, and 40°C for at least 2 days. Thereafter, the nascent films were dried in a vacuum oven at 70°C for 24 hours to eliminate residual solvent and unreacted PEO-azide. This process also promotes further reacting between the organic and inorganic components as well as facilitating condensation. After the drying process, the dried films were removed from the Teflon dish and kept in a dry environment. The nascent films were heat treated at temperatures ranging from 100°C to 200°C. Scheme 4 depicts possible chemical reactions.

Scheme 4







The ratio of PEO-azide to PEO/silica varied with respect to the PEO/silica polymer. From Table 3, increments in H_2 , N_2 , and CO_2 permeability were observed when the amount of ethylene oxide units increased. All tested gas permeabilities increased as a function of temperature. With increased temperatures, polymer chain rigidity is reduced. Hence, gas permeability will increase.

Table 3

**CO₂/H₂ and CO₂/N₂ separation capabilities of
PEO-GOTMS/PEO-azide membranes at
different temperatures**

Sample Name	Temperature (°C)	H ₂ permeability (Barrer)	N ₂ permeability (Barrer)	CO ₂ permeability (Barrer)	CO ₂ /H ₂ selectivity	CO ₂ /N ₂ selectivity
GPA312 Pristine	35	46.3	23.0	529	11.4	23.0
	40	174.0	38.4	1434	8.2	37.3
	45	209.2	47.0	1554	7.4	33.1
GPA312 140°C vacuum 12hrs	35	180.8	38.0	898	5.0	23.6
	40	259.0	56.6	2365	9.1	41.8
	45	336.9	76.1	2778	8.2	36.5

GPA312: GOTMS:PEO:PEO-azide molar ratio $\approx$ 3:1:1

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OTHER EMBODIMENTS

All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose. Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

WHAT IS CLAIMED IS:**1. A monomer comprising:**

a poly(alkylene) oxide backbone having 20 to 1000 carbon atoms and 10 to 500 oxygen atoms, the carbon/oxygen ratio being 1:1 to 10:1;

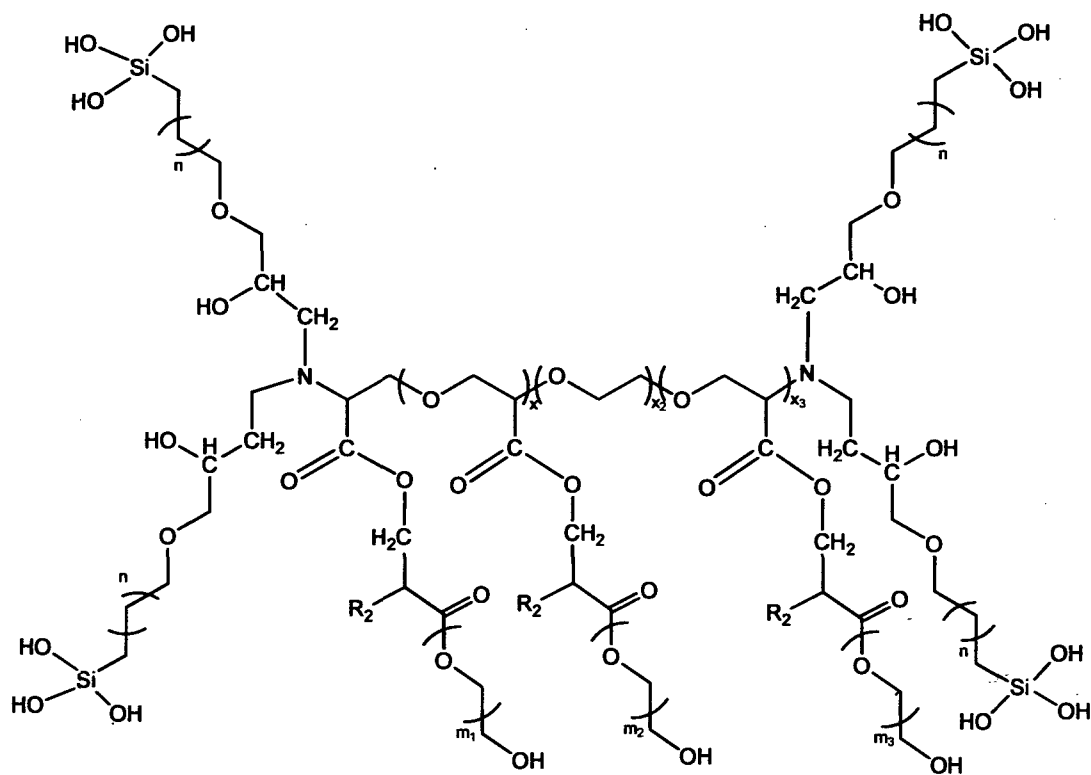
5 one to one hundred poly(alkylene) oxide side chains attached to the backbone, wherein each chain has 10 to 500 carbon atoms and 5 to 250 oxygen atoms, the carbon/oxygen ratio being 1:1 to 10:1; and

one to eight cross-linking groups also attached to the backbone, each cross linking group having two to four binding moieties,

10 whereby the monomer is capable of cross-linking other monomers having the same structural features to form a polymer via its binding moieties and the binding moieties of the other monomers.

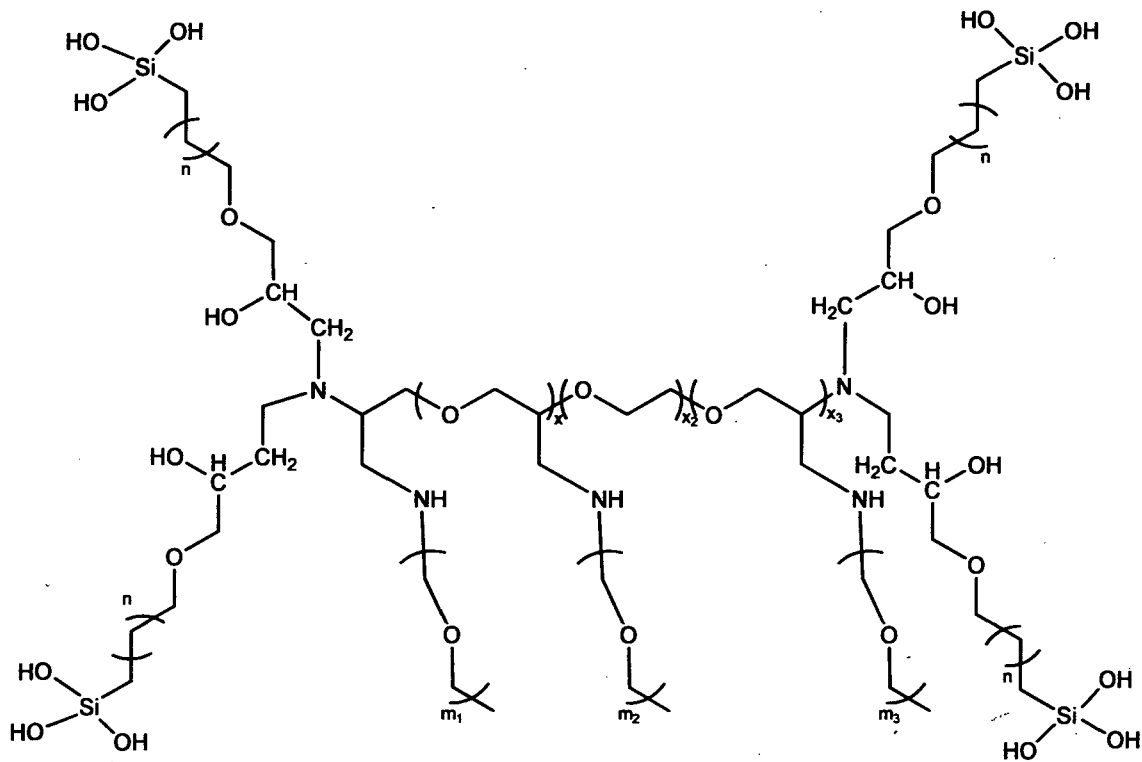
15 2. The monomer of claim 1, wherein one to three cross linking groups attach to each end of the backbone.

3. The monomer of claim 2, wherein the monomer is of the formula:



wherein each of m_1 , m_2 , and m_3 , independently, is 5 to 500; each n , independently, is 1 to
 5 20; each of x , x_2 , and x_3 , independently, is 2 to 500; and R_2 is a hydrogen or an alkyl
 group.

4. The monomer of claim 2, wherein the monomer is of the formula:



wherein each of m_1 , m_2 , and m_3 , independently, is 5 to 500; each n , independently, is 1 to 10; and each of x , x_2 , and x_3 , independently, is 2 to 500.

5

5. A polymer comprising a plurality of monomers that are cross-linked to each other, wherein each of the monomers, independently, is a monomer of claim 1.

10 6. The polymer of claim 5, wherein each of the monomers, independently, is a monomer of claim 3.

7. The polymer of claim 5, wherein each of the monomers, independently, is a monomer of claim 4.

15

8. A method of preparing a branched cross linker-containing poly(alkylene) oxide chain, the method comprising reacting a branched poly(alkylene) oxide backbone, having a first reactive group and a second reactive group on the backbone, with two to eight cross-linkers, each having a third reactive group, whereby the third reactive group of a cross
5 linker covalently bonds with the first reactive group and the third reactive group of another cross linker covalently bonds with the second reactive group to form a branched cross linker-containing poly(alkylene) oxide chain, wherein each of the cross linkers has two to four binding moieties

10 9. A method of preparing a branched cross linker-containing poly(alkylene) oxide chain, the method comprising:

reacting a poly(alkylene) oxide backbone, having a first reactive group and a second reactive group, with two to eight cross linkers, each having

a third reactive, whereby the third reactive group of a cross linker covalently
15 bonds with the first reactive group and the third reactive group of another cross linker covalently bonds with the second reactive group to form a cross linker-containing poly(alkylene) oxide backbone; wherein each of the cross linkers has two to four binding moieties; and

generating free radicals on the cross linker-containing poly(alkylene) oxide
20 backbone and reacting poly(alkylene) oxide side chains, each having a fourth reactive group at one end, with the cross linker-containing poly(alkylene) oxide backbone to form a branched cross linker-containing poly(alkylene) oxide chain, via covalent bonding of the fourth reactive group to the cross linker-containing poly(alkylene) oxide backbone.

25 10. A method of preparing a polymer, the method comprising reacting a plurality of branched cross linker-containing poly(alkylene) oxide chains, prepared by the method of claim 8 or claim 9, to form a polymer via bonding between binding moieties in one chain to binding moieties in other chains.

30 11. A method of altering the composition of a gaseous mixture, the method comprising:

providing a membrane formed of the polymer of claim 5, and
passing through the membrane a gaseous mixture, containing at least a first gas
and at least a second gas, wherein the first gas is selected from the group containing H₂,
N₂, CH₄, O₂, and C₃H₈, and the second gas is selected from the group containing CO₂,
5 H₂S, CO, and H₂O.

12. The method of claim 11, wherein the first gas is H₂ and the second gas is CO₂.

13. A method of preparing a membrane, the method comprising:

10 preparing a solution containing poly(alkylene) oxide backbones, poly(alkylene)
oxide chains, and a solvent, the backbones and the chains being dispersed in the solvent,
wherein each of the backbones has two to eight cross linking groups and each of the cross
linking groups has two to four binding moieties;
providing a layer of the solution;
15 cross linking the backbones via covalent bonding between binding moieties in one
backbone to binding moieties in other backbones; and
removing the solvent to form a membrane;
whereby the chains are blended with the cross linked backbones.

20 14. A method of preparing a membrane, the method comprising:

preparing a solution containing poly(alkylene) oxide backbones, poly(alkylene)
oxide chains, the backbones and the side chains being dispersed in the solvent, wherein
each of the backbones has two to eight cross linking groups, each of cross linking groups
has two to four binding moieties and each of the chains has a reactive group at an end;
25 providing a layer of the solution;
cross linking the backbones via covalent bonding between binding moieties in one
backbone to binding moieties in other backbones;
removing the solvent to obtain the membrane; and
generating free radicals on the poly(alkylene) oxide backbones, whereby the
30 chains, via the reactive groups, covalently bond to the backbones.

15. A membrane prepared by the method of claim 13.
16. A membrane prepared by the method of claim 14.
- 5 17. A method of altering the composition of a gaseous mixture, the method comprising passing a gaseous mixture through the membrane of claim 13 or 14, wherein the mixture contains at least a first gas is selected from the group containing H_2 , N_2 , CH_4 , O_2 , and C_3H_8 , and the second gas is selected from the group containing CO_2 , H_2S , CO , and H_2O .
- 10 18. The method of claim 17, wherein the first gas is H_2 and the second gas is CO_2 .