

HIGHLY SELECTIVE POLYNORBORNENE HOMOPOLYMER MEMBRANES FOR NATURAL GAS UPGRADING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Patent Application 15/057,894 filed March 1, 2016, which is incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to norbornene homopolymer membranes and their ability to separate natural gas molecules.

BACKGROUND

[0003] The natural gas used by consumers is composed almost entirely of methane. However, natural gas found at the wellhead, although still composed primarily of methane, is by no means as pure. Natural gas is typically isolated from three different sources: oil wells, gas wells and condensate well, but whatever the source of the natural gas, it commonly exists in mixtures with other hydrocarbons; principally ethane, propane, butane, and pentanes. Each of these hydrocarbons has a similar size and polarity. Pentane, a larger hydrocarbon, is more easily separated, but for the smaller hydrocarbons, separation is a challenging endeavor.

[0004] Most membranes used in the gas separation field are derived from glassy polymers and are generally unacceptable for heavy hydrocarbon separations. Most glassy polymers have high permeation of methane relative to propane, butane, and other gases, and these glassy polymers are not sufficiently selective to discriminate between heavy hydrocarbons and methane. Glassy polymer membranes have been used to effectively separate oxygen and nitrogen in air samples, and have also been used to separate butanol from other biofuels; however, these glassy polymer membranes achieve low hydrocarbon selectivity and thus do not provide sufficient separation for natural gas upgrading applications. In contrast, rubbery polymers, such as polydimethylsiloxane (PDMS), have high permeability, but generally have a lower selectivity. Moreover, the glassy polymer membranes tend to show a decrease in performance due to aging. Aging occurs from collapse of free volume, which tends to cause lower permeability.

SUMMARY

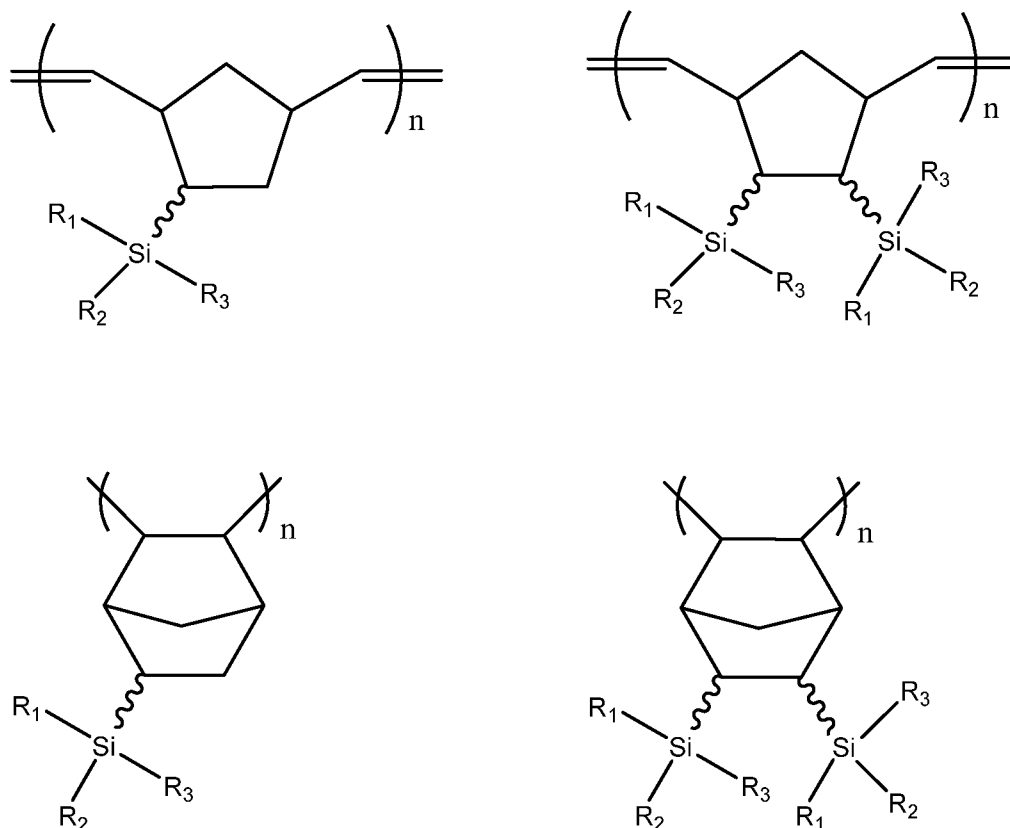
[0005] Accordingly, there is a continual need for improved natural gas upgrading membranes which achieve high selectivity, while maintaining suitable permeability, and a long membrane life.

[0006] Embodiments of the present disclosure are directed to crosslinked alkoxysilyl polynorbornene homopolymer formulations, methods of making crosslinked alkoxysilyl polynorbornene homopolymer formulations, and methods of membranes incorporating these crosslinked alkoxysilyl norbornene homopolymer formulations, where these norbornene homopolymer membranes demonstrate a high selectivity, suitable permeability, and greater resistance to aging and plasticization, especially in natural gas upgrading applications. Membranes are characteristically subject to tradeoff relationships, where heightened selectivity is accompanied by undesirable decreases in permeability. However, the pendant alkoxysilyl moieties of the present crosslinked alkoxysilyl polynorbornene homopolymer formulations maintain high permeability while achieving greater selectivities, which is lacking in trimethylsilyl substituted polymers. Further, prior polynorbornenes utilized in natural gas upgrading applications achieve a lower maximum selectivity for propane over methane (C_3H_8/CH_4) of 3 under pure gas conditions at 50 psi, whereas the present crosslinked alkoxysilyl norbornene homopolymer membranes may yield at least double that selectivity performance at similar conditions.

[0007] In accordance with one embodiment, a method of making a crosslinked alkoxysilyl polynorbornene homopolymer comprising polymerizing a norbornene monomer, having an alkoxysilyl moiety, in the presence of a catalyst to produce an alkoxysilyl modified polynorbornene homopolymer, and producing a crosslinked alkoxysilyl polynorbornene homopolymer through sol-gel initiated crosslinking of the alkoxysilyl modified polynorbornene homopolymer.

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In accordance with another embodiment, a formulation comprising a crosslinked alkoxy silyl polynorbornene homopolymer is provided having either of the following structures:



In this case, R1 is an alkyl, an alkoxy, or OSiR₄R₅, R2 is an alkyl, an alkoxy, or OSiR₄R₅, R3 is an alkyl, an alkoxy, or OSiR₄R₅, R4 is an alkyl or an alkoxy, R5 is an alkyl or an alkoxy, and n is at least one, with the requirement that at least one of R1, R2, and R3, is an alkoxy or an alkoxy siloxane, such as OSiR₄R₅. Moreover, the cross-linking is characterized by 10% to 100% by weight gel content.

[0008] Additional features and advantages of the embodiments will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a graphical illustration of the selectivity yielded by different crosslinked ethoxysilyl polynorbornene homopolymers [ROMP-SiMe₂OEt, ROMP-SiMe(OEt)₂, ROMP-Si(OEt)₃] produced by ring opening metathesis polymerization (ROMP) in comparison to a non-alkoxylated polynorbornene homopolymer produced by ROMP (ROMP-SiMe₃).

[0010] FIG. 2 is a graphical illustration of the selectivity yielded by different crosslinked ethoxysilyl polynorbornene homopolymers [APN-SiMe₂OEt, APN-SiMe(OEt)₂, APN-Si(OEt)₃] produced by addition polymerization (APN) in comparison to a non-alkoxylated polynorbornene homopolymer produced by APN (APN-SiMe₃).

[0011] FIG. 3 is a graphical illustration of Wide Angle X-Ray Diffraction (WAXRD) patterns of different crosslinked ethoxysilyl polynorbornene homopolymers [ROMP-SiMe₂OEt, ROMP-SiMe(OEt)₂, ROMP-Si(OEt)₃] produced by ring opening metathesis polymerization (ROMP) in comparison to a non-alkoxylated polynorbornene homopolymer produced by ROMP (ROMP-SiMe₃).

[0012] FIG. 4 is a graphical illustration of WAXRD patterns of different crosslinked ethoxysilyl polynorbornene homopolymers [APN-SiMe₂OEt, APN-SiMe(OEt)₂, APN-Si(OEt)₃] produced by addition polymerization (APN) in comparison to a non-alkoxylated polynorbornene homopolymer produced by APN (APN-SiMe₃).

[0013] FIG. 5 is a bar chart depicting the increase in gel fraction (%) and crosslinking in APN or ROMP, when further conducting the sol-gel initiated crosslinking in acid catalyzed conditions, in this case acetic acid.

[0014] The embodiments set forth in the drawings are illustrative in nature and not intended to be limiting to the claims. Moreover, individual features of the drawings will be more fully apparent and understood in view of the detailed description.

DETAILED DESCRIPTION

[0015] Embodiments of the present disclosure are directed to crosslinked alkoxysilyl polynorbornene homopolymer formulations and membranes including these crosslinked alkoxysilyl polynorbornene homopolymer formulations, where the membranes have improved selectivity separating smaller hydrocarbons, such as methane, ethane, propane and butane, from a heavy hydrocarbon stream.

[0016] As used herein, “homopolymer” means that the polymer molecule is produced from only one monomer, specifically the norbornene monomers discussed below, and thus does not encompass copolymers comprising additional comonomers. Though, this work could utilize novel copolymerizations to increase free volume and thus the performance of the resulting membranes. That being said, it is contemplated in some embodiments to blend additional components such as additional polymers or additives with the crosslinked alkoxysilyl polynorbornene homopolymer formulation in the membrane. Such additives could comprise silane small molecule derivatives, which further influence the so-gel chemistry. Whereas, high engineered additives, such as carbon nanotubes, graphene, or other molecules with metal organic frameworks, would be beneficial in increasing the homopolymer’s transport properties.

[0017] As used herein, “selectivity” refers to the separation of larger hydrocarbons in comparison to methane. While the following discussion and examples discuss selectivity or propane relative to methane, “selectivity” as used herein may also encompass other larger hydrocarbons such as butane relative to methane. Pure gas selectivity at 50 psi has been as high as 53 for butane to methane, which is substantially higher than propane relative to methane selectivity.

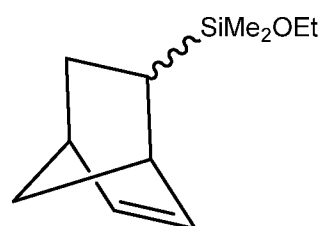
[0018] Without being bound by theory, the alkoxysilyl groups of the crosslinked alkoxysilyl polynorbornene homopolymer formulations may provide improved performance to the membrane by increasing the free volume between polymer chains by enhancing steric interactions, as well as promoting gas diffusion due to their high mobility and flexibility. Additionally, the alkoxysilyl containing norbornene polymers are crosslinkable, which offers stabilized performance against aging in long-term applications, while also further increasing the selectivity of the membranes.

[0019] Furthermore, increasing the alkoxy content has provided improved selectivity in membranes used in natural gas upgrading, and specifically for the separation of heavy hydrocarbons (ethane, propane, butane) from methane. As described further below, the membrane selectivities of propane to methane may be 8 or higher under pure gas conditions at 50 psi.

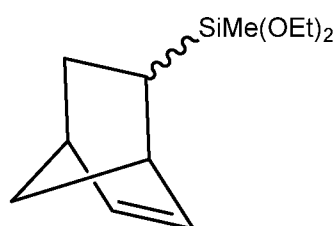
[0020] The crosslinked alkoxysilyl polynorbornene homopolymer may be produced by polymerizing a norbornene monomer comprising an alkoxysilyl moiety in the presence of a catalyst to produce an alkoxysilyl modified polynorbornene homopolymer. Then, the crosslinked alkoxysilyl polynorbornene homopolymer may be produced through sol-gel initiated crosslinking of the alkoxysilyl modified polynorbornene homopolymer. Various reaction conditions are contemplated for the sol-gel initiated crosslinking. In one or more embodiments, the sol-gel process may be initiated at ambient conditions, or acid-catalyzed conditions. For example, the sol-gel initiated crosslinking involves hydrolysis in water or exposure to the atmosphere. Moreover, the degree of crosslinking may be further increased in acid-catalyzed conditions. For example, acids, such as acetic acid, may greatly increase the crosslinking of the alkoxy moieties. While the sol-gel crosslinking of the alkoxysilyl modified polynorbornene homopolymer may be analogized to the crosslinking of ethoxy moieties in a tetraethylorthosilicate (TEOS) compound, it is contemplated that multiple alkoxy alternatives to the ethoxy may be utilized.

[0021] In accordance with the present disclosure, the norbornene monomer may comprise one to nine alkoxysilyl groups. For example and not by way of limitation as shown below, the norbornene monomers may include methyldiethoxysilylnorbornene (Structure 1), dimethylethoxysilylnorbornene (Structure 2), and triethoxysilylnorbornene (Structure 3). In some embodiments, more alkoxysilyl substituents may be present. For example, instead of the methyl or alkoxy groups bonded to the silica atom, an alkoxysiloxane substituent may be bonded to the silica atom, (i.e. $[\text{OSi}(\text{OMe})_3]_3$) (Structure 4). Additionally, more than one moiety may be present on the bicyclic ring structure (Structure 5)

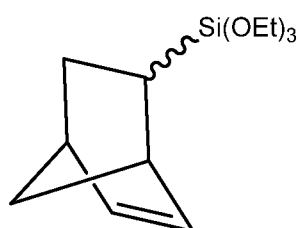
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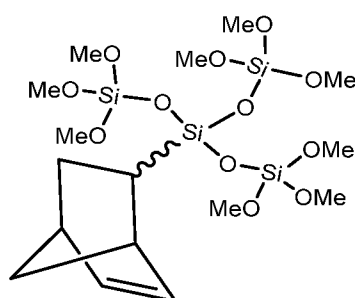
(Structure 1)



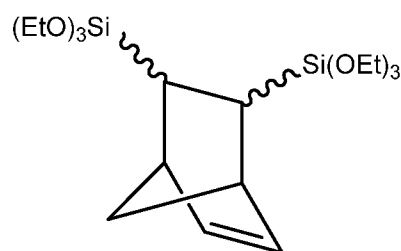
(Structure 2)



(Structure 3)



(Structure 4)



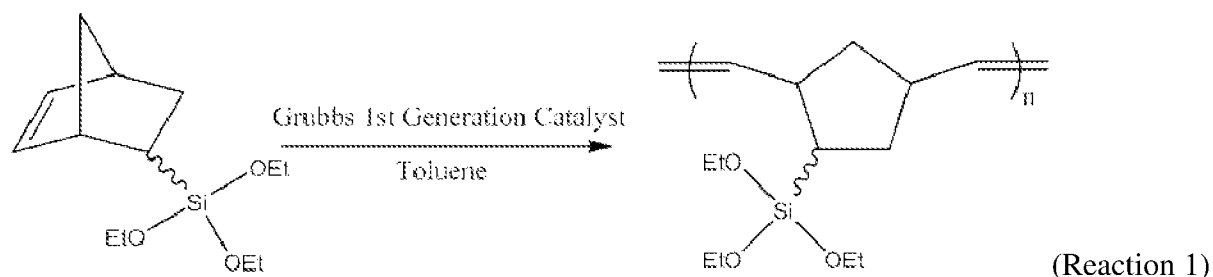
(Structure 5)

[0022] Various polymerization techniques are contemplated. The polymerization technique may include ring-opening metathesis polymerization (ROMP) and addition polymerization as illustrated further as follows.

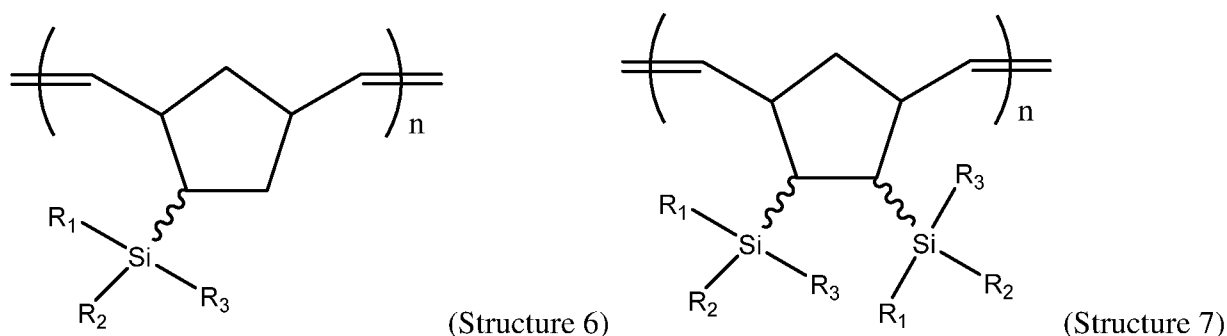
[0023] In another embodiment, the polymerizing step may include a ROMP catalyst. The ROMP catalyst may include a Grubbs catalyst, which is a transition metal complex. In one or more embodiments, the Grubbs catalyst is a Grubbs 1st Generation catalyst, or any later generation of Grubbs catalyst. In one embodiment, the catalyst is a ruthenium catalyst. Optionally, the catalyst may be provided with a carrier or solvent, such as toluene. For example, the ROMP catalyst is a Grubbs 1st Generation catalyst, and may undergo the reaction depicted below.

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[0024] Below is a sample ROMP Process utilizing triethoxysilylnorbornene monomer (further shown in Structure 3) and a Grubbs 1st Generation catalyst (Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium):



[0025] In addition to the triethoxysilyl polynorbornene homopolymer produced in Reaction 1 shown previously, the polynorbornene homopolymer of the ROMP process may have the following structure depicted in Structure 6 as follows:

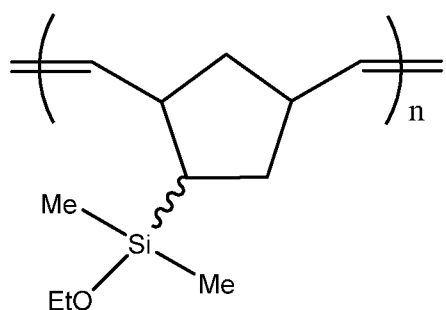


[0026] In the alkoxy-modified cyclopentane structure of Structure 6 and Structure 7, the R₁ is an alkyl, an alkoxy, or OSiR₄R₅, R₂ is an alkyl, an alkoxy, or OSiR₄R₅, R₃ is an alkyl, an alkoxy or OSiR₄R₅, R₄ is an alkyl or an alkoxy, R₅ is an alkyl or an alkoxy, and n is at least one, with the requirement that at least one of R₁, R₂, and R₃ is an alkoxy. In further embodiments, at least two and a maximum of all three of R₁, R₂, and R₃ is an alkoxy or an alkoxy-siloxane substituent (i.e. OSiR₄R₅), where the at least two alkoxy groups comprise the same or a different alkyl moiety.

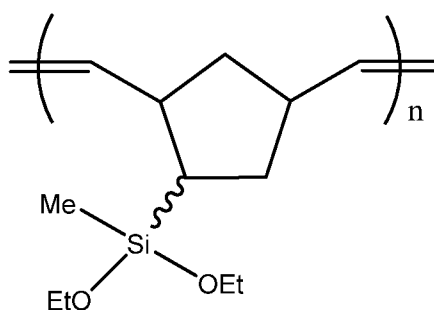
[0027] Various alkoxy groups are contemplated. In one embodiment, alkoxy groups are C₁-C₆ alkoxy moieties. For example, the alkoxy or alkoxy-siloxane moieties in R₁-R₃ may include

from one to nine of ethoxy groups, methoxy groups, propoxy groups, isopropoxy groups, isobutoxy groups, tert-butoxy groups, or combinations thereof.

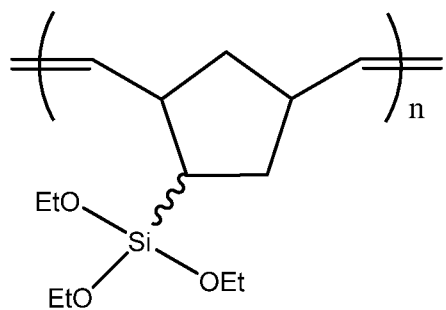
[0028] For example and not by way of limitation, the polynorbornene homopolymers produced from the ROMP process may include the specific structures depicted as follows: ROMP-SiMe₂OEt (Structure 8), ROMP-SiMe(OEt)₂ (Structure 9), and ROMP-SiMe(OEt)₃, (Structure 10).



(Structure 8)



(Structure 9)



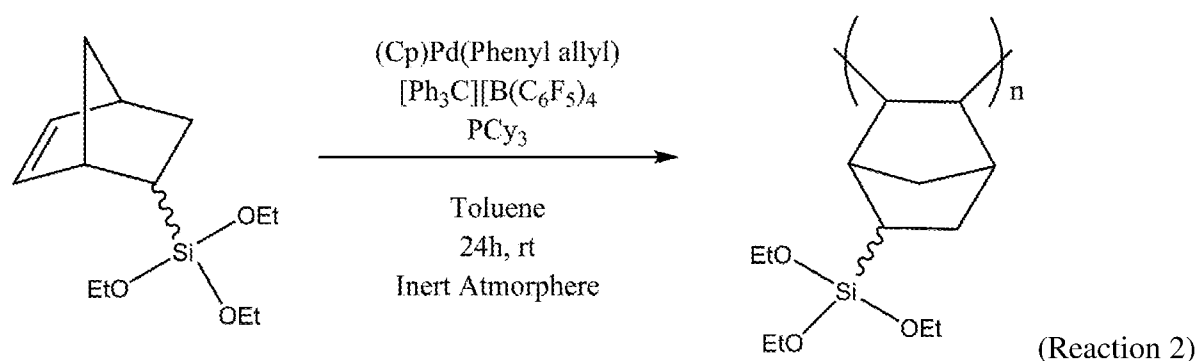
(Structure 10)

[0029] Alternatively, the polymerizing step may be an addition polymerization process which utilizes an addition polymerization catalyst to polymerize the alkoxy silyl norbornene monomers. The addition polymerization catalyst may include at least one transition metal catalyst. In one or more embodiments, the transition metal catalyst may comprise nickel, palladium, titanium, zirconium, chromium, vanadium, or combinations thereof. In yet another embodiment, the transition metal catalyst may be a late-transition metal. In one example, the addition polymerization catalyst may be a palladium metallocene catalyst. In further embodiments, the addition polymerization catalyst may be a mixed catalyst comprising the transition metal catalyst and other catalyst components. In one or more embodiments, the addition catalyst may comprise a palladium metallocene catalyst, a trityl borate, and a phosphine. Without being limited to

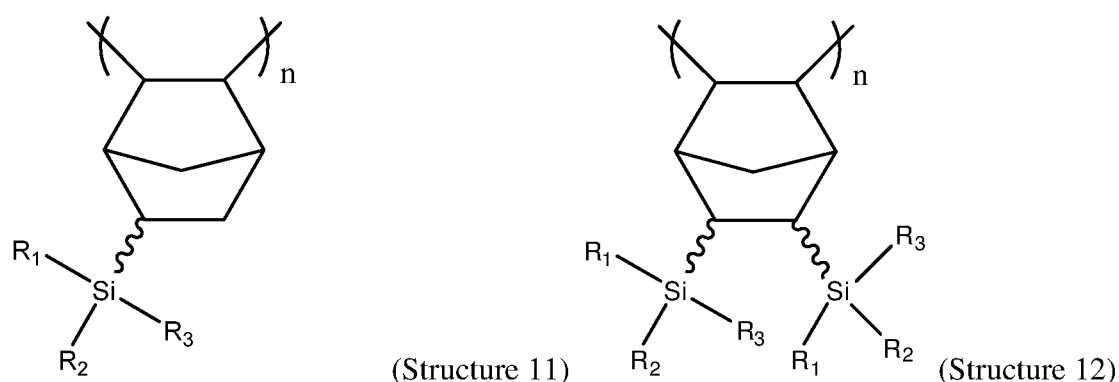
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theory, this mixed catalyst is suitable because it has sufficient activity able to overcome the steric bulk of the norbornene monomer. Optionally, the addition catalyst may be mixed in a solvent solution, for example, toluene.

[0030] Below is a sample addition polymerization process utilizing triethoxysilylnorbornene monomer (further shown in Structure 3) and a mixed catalyst comprising a palladium metallocene catalyst, a phosphine and a trityl borate.



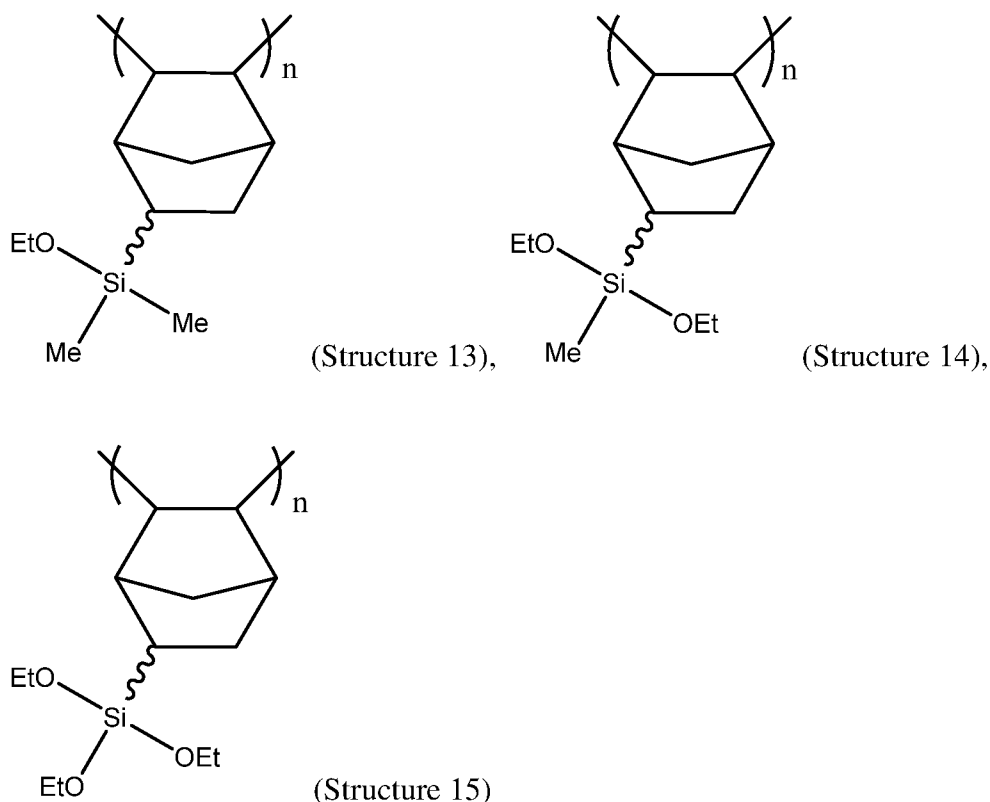
[0031] In addition to the triethoxysilyl polynorbornene homopolymer produced in Reaction 2 shown previously, the polynorbornene homopolymer of the additional polymerization process may have the following bicyclic structure depicted in Structure 6 as follows:



[0032] In the alkoxyisilyl modified bicyclic structure of Structure 11 and Structure 12, the R1 is an alkyl, an alkoxy, or OSiR₄R₅, R2 is an alkyl, an alkoxy, or OSiR₄R₅, R3 is an alkyl, an alkoxy, or OSiR₄R₅, R4 is an alkyl or an alkoxy, R5 is an alkyl or an alkoxy, and n is at least one, with the requirement that at least one of R1, R2, and R3 is an alkoxy or alkoxyisiloxane. In

further embodiments, at least two of R1, R2, R3, R4 and R5 is an alkoxy or an alkoxy siloxane substituent (similar to moiety in Structure 4), where at least two alkoxy groups comprise the same or a different alkyl moiety.

[0033] For example and not by way of limitation, the alkoxy silyl polynorbornene homopolymers produced from the additional polymerization process may include the specific structures depicted as follows: APN-SiMe₂OEt (Structure 13), APN-SiMe(OEt)₂ (Structure 14), and APN-Si(OEt)₃ (Structure 15).



[0034] While the structure of alkoxy silyl polynorbornene homopolymers differ slightly when produced by ROMP or APN, the alkoxy silyl moiety is common to both. In one or more embodiments, the alkoxy silyl polynorbornene homopolymer chain may include from 10% by weight to 80 % by weight alkoxy, or from 15 to 75 % by weight alkoxy, or from 20 % to 60 by weight alkoxy depending on the number of alkoxy moieties attached to the silicon.

[0035] In one or more embodiments, the crosslinked alkoxysilyl polynorbornene homopolymer may comprise a molecular weight distribution (MWD) from 1 to 3, where MWD is defined as M_w/M_n with M_w being a weight average molecular weight and M_n being a number average molecular weight. In further embodiments, the crosslinked alkoxysilyl polynorbornene homopolymer may include an MWD from 1 to 2.

[0036] As stated previously, the alkoxysilyl groups of the alkoxysilyl polynorbornene homopolymers have controllable crosslinking functionalities. Without being limited to theory, crosslinking may often occur prematurely during synthesis, resulting in polymers that cannot be processed into membrane form. However, the crosslinking of the present alkoxysilyl polynorbornene homopolymer embodiments may be controlled such the alkoxysilyl polynorbornene homopolymer is synthesized, precipitated, and cast into film form before crosslinking occurs. As stated previously, crosslinking occurs in the final film state by exposure to water or, in some cases, prolonged exposure to atmosphere in ambient conditions. Referring to FIG. 5, the degree of crosslinking when the alkoxysilyl polynorbornene homopolymer is treated with an acid, such as acetic acid. In one or more embodiments, the crosslinking of the crosslinked alkoxysilyl polynorbornene homopolymer may be characterized by 10% to 100% by weight gel content, or 20 to 100% by weight gel content.

[0037] As stated previously, one of the key features of the present membrane is higher selectivity between heavy hydrocarbons and methane. In order for a membrane to be effective at separating small molecules, the pore sizes in the membrane must be controlled as well. Gas permeation studies were used to determine the selectivity. Pure gas permeability coefficients were measured using a constant volume, variable pressure technique. The upstream side of the membrane was constructed using stainless-steel Swagelok® tubing and tube fittings. The downstream side consisted of mostly welded Swagelok® tubing and VCR fittings. A stainless-steel, high pressure filter holder (Millipore, Billerica, MA) was used to house the membrane. Permeability measurements were taken using a feed pressure between 50 – 100 psi at room temperature (23 – 25 °C). The downstream, or permeate pressure, was maintained at less than 50 Torr. Establishment of permeation steady-state was verified using the time-lag method, where 14x the diffusion time-lag was taken as the effective steady-state. System pressure was

measured using Baratron absolute pressure transducers (MKS Instruments, Billerica MA) and recorded using Labview Software.

[0038] The permeability coefficient is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness. The membrane thickness can range from 50 to 150 microns. The membrane thickness can be significantly lower and can be less than 1 micron. The pure gas permeability coefficients are calculated using a constant volume/variable pressure technique. The permeability coefficient is calculated using the following equation:

$$\text{[0039]} \quad P_i = (n_i * l) / \Delta f \quad (\text{Equation 1})$$

[0040] Where n is the molar flux, l is the membrane thickness and Δf is the fugacity difference across the membrane. Using a fugacity difference, rather than a partial pressure difference, accounts for gas phase non-idealities in the feed stream, which can significantly affect the permeability values of hydrocarbon gases. Fugacity coefficients are calculated using the Peng-Robinson equation of state. Ideal selectivity was calculated by the following equation:

$$\text{[0041]} \quad \alpha = P_i / P_j \quad (\text{Equation 2})$$

[0042] As shown in FIG. 1, the addition polymerized alkoxysilyl polynorbornene homopolymers [APN-SiMe₂OEt, APN-SiMe(OEt)₂, APN-Si(OEt)₃] all achieve propane/methane selectivity between about 6 to about 9 under pure gas conditions at 50 psi, with most alkoxysilyl polynorbornenes achieving a selectivity of about 7 to about 8. In contrast, the addition polymerized polynorbornene without an alkoxy (APN-SiMe₃) achieved a selectivity of only about 3. Referring to FIG. 2, while ROMP alkoxysilyl polynorbornene homopolymers [ROMP-SiMe₂OEt, ROMP-SiMe(OEt)₂, ROMP-Si(OEt)₃] achieve lower selectivity than the addition polymerized alkoxysilyl polynorbornene homopolymers [APN-SiMe₂OEt, APN-SiMe(OEt)₂, APN-Si(OEt)₃] of FIG. 1, the selectivity is at least 3 times the selectivity of the ROMP polynorbornene homopolymers without an alkoxy (ROMP-SiMe₃).

[0043] As stated previously, selectivity correlates at least in part to interchain packing. Wide Angle X-ray Diffraction (WAXRD) is most often used in the analysis of crystalline small molecules and crystalline polymers. Most useful membranes in gas separations are largely amorphous and therefore few studies relate the data obtained in WAXRD patterns to permeation properties. However, by relating the scattering angle to interchain distances via Bragg's law, the interchain distances may be calculated from the WAXRD peaks shown (denoted by asterisks above the peak in FIGS. 3 and 4).

[0044] Interchain distances are denoted as $(d_B/d_{ic}) = (\text{Bragg's distance/interchain correction distance}) = ([\lambda/2 \sin \theta]/[1.22 \lambda/2 \sin \theta])$.

[0045] Referring for illustration to the embodiments of FIGS. 3 and 4, the crosslinked alkoxysilyl polynorbornene homopolymers include at least a first chain packing region and a second chain packing region (illustrated by asterisks), where the first chain packing region is defined by a first interchain distance and the second chain packing region is defined by a second interchain distance, the first interchain distance being smaller than the second interchain distance, where the first interchain distance and second interchain distance are calculated from Bragg's Law for angle peaks measured by WAXRD. In another embodiment, the crosslinked alkoxysilyl polynorbornene homopolymers may further comprise a third packing region defined by a third interchain distance, the third interchain distance being larger than the first interchain distance and second interchain distance. In yet another embodiment, the crosslinked alkoxysilyl polynorbornene homopolymers may further comprise a fourth packing region defined by a fourth interchain distance, the fourth interchain distance being smaller than the first, second, and third interchain distances.

[0046] The features of the present embodiments will be further illustrated in the Examples which follow.

[0047] Examples

[0048] *Ring-opening metathesis polymerization triethoxysilylnorbornene (ROMP –Si(OEt)₃ synthesis:*

[0049] Referring to Reaction 1 for illustration, in a glovebox, a 30 milliliter (mL) vial was charged with 03.85 g of as received triethoxysilylnorbornene (0.05 molar (M), 1.51 millimoles (mmol)) and 29 mL of dry deoxygenated toluene. In a separate vial, 2.5 milligrams (mg) of Grubb's first generation catalyst, containing Ruthenium, (.003 mmol) was dissolved in 2 mL of dry toluene to create a stock catalyst solution. Finally, 1.0 mL of the catalyst solution was added to the stirring norbornene solution to initiate polymerization. After 24 hours ethyl vinyl ether (0.431 mL, 4.51 mmol) was added to terminate the polymerization, and the solution continued to stir. After another 24 hours, the solvent was removed under vacuum in the glovebox until the sample volume was approximately 5 mL, where the sample became a viscous liquid. The viscous solution was precipitated dropwise into stirring alcohol (500 mL). Upon precipitation a fibrous polymer was obtained in a cloudy supernatant. The polymer was dried to constant weight and isolated as an off-white solid.

[0050] *Addition polymerization triethoxysilylnorbornene (APN-Si(OEt)₃) synthesis:*

[0051] Referring to Reaction 2 for illustration, under nitrogen, a 30 mL vial was charged with 1.541 g of as received triethoxysilylnorbornene (6.01 mmol) and 29.7 mL of dry, deoxygenated toluene (0.2 M). In three separate vials, 0.34 mg tricyclohexylphosphine (00012 mmol) was dissolved in 1 mL of toluene, while 0.35 mg of cyclopentadienyl-(1,2,3-n)-1-phenyl-2-propenyl palladium (II) (0.0012 mmol) was dissolved in 1 mL of toluene, and 1.11 mg trityl tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (0.0012 mmol) was dissolved in 1 mL of toluene. 0.2 mL of the solution containing the palladium catalyst was mixed with 0.2 mL of the phosphine solution, and then 0.2 mL of the trityl borate solution was added to the 0.4 mL of palladium and phosphine. Afterwards, 0.3 mL of the mixed catalyst solution was added to the norbornene solution. The reaction vessel was sealed and brought out of the glove box to heat and stir at 40 degrees Celsius (C) for 24 hour, where it became yellow and viscous. After 24 hours, the solution was precipitated in 1000 mL of acetone dropwise, which immediately formed small white polymer beads stirring in the acetone. The white polymer was collected via filtration and dried under reduced pressure at room temperature.

[0052] Addition polymerization triethoxysilylnorbornene (APN-Si(OEt)₃) casting:

[0053] A 0.5 gram (g) sample of triethoxy polymer was dissolved in 10 mL of toluene and stirred until completely dissolved. The solution was then filtered with a 0.45 microliter (μL) syringe filters under dry, inert conditions in a glovebox. A 10 mL filtered polymer solution with a 5 w/v % concentration was poured into a 10 centimeter (cm) diameter PFA mold on a level surface. The PFA mold was covered to slow the rate of evaporation, and the film was allowed to dry overnight. Polymer film was removed from the PFA mold and dried to constant weight under vacuum. The obtained films were transparent, ductile and colorless.

[0054] Table 1

Polymer	(2θ) ₁ , deg	(d _B /d _{ic}) ₁	(2θ) ₂ , deg	(d _B /d _{ic}) ₂	(2θ) ₃ , deg	(d _B /d _{ic}) ₃	(2θ) ₄ , deg	(d _B /d _{ic}) ₄
ROMP-SiMe ₃	-	-	-	-	15.5	5.7/7.0	-	-
ROMP-SiMe ₂ OEt	-	-	-	-	12.3	7.2/8.8	18.4	4.8/5.9
ROMP-SiMe(OEt) ₂	4.3	20.4/24.9	-	-	13.3	6.7/8.2	16.9	5.2/6.3
ROMP-Si(OEt) ₃	2.7	32.4/39.5	-	-	12.4	7.1/8.7	18.6	4.8/5.9
APN-SiMe ₃	-	-	7.4	12.0/14.6	15.5	5.7/7.0	-	-
APN-SiMe ₃ (Finkelstein et. al.)	-	-	6.5	13.6/16.6	15.5	5.7/7.0	-	-
APN-SiMe ₂ OEt	2.2	40.9/49.9	7.1	12.5/15.3	15.4	5.8/7.1	-	-
APN-SiMe(OEt) ₂	-	-	7.1	12.4/15.1	15.4	5.7/7.0	-	-
APN-Si(OEt) ₃	2.5	34.9/42.6	6.6	13.4/16.3	13.9	6.4/7.8	21.0	4.2/5.1

[0055] Referring to FIG. 4 and Table 1 above, ROMP-SiMe₃ shows only one peak representing a chain packing of (5.7/7.0) Å, which while relatively high is consistent with many diffusion controlled gas separation membranes such as polysulfone or polyimide. Upon ethoxy substitution this peak starts to broaden out in ROMP-SiMe₂OEt to form two peaks equaling

(7.2/8.8) Å and (4.8/5.9) Å. This larger interchain peak is indicative of the high free volume between polymer chains, which allows for solubility-controlled permeation since the chain packing is too large to effectively discriminate between gas molecules. The smaller interchain peak may arise due to the crosslinking of the ethoxy-containing polymers, which is a mechanism for closer packing between polymer chains.

[0056] This trend also continues in ROMP-SiMe(OEt)₂ and ROMP-Si(OEt)₃, although in these two polymers a third region of very loose chain packing begins to emerge, (20.4/24.9) Å and (32.4/39.5) Å respectively. It is assumed that these regions will even further promote the loss of diffusivity-controlled selectivity and the emergence of solubility-controlled selectivity.

[0057] Referring to FIG. 3 and Table 1 above, the methyl-substituted polynorbornene APN-SiMe₃ is already known in the literature to be a solubility-selective material. This polymer has a bimodal chain packing distribution with a large distant chain-packing region as (13.6/16.6) Å, which was calculated under Bragg's law to be (12.0/14.6) Å. This loose chain-packing accounts for the lack of diffusivity-selectivity in the addition-type polymers. The low scattering angle peak generally shifted to even lower angles as a function of increasing ethoxy substitution, finally reaching (13.4/16.3) Å in the APN-Si(OEt)₃ polymer. One notable exception in this trend was that APN-SiMe(OEt)₂ (12.4/15.1) actually had increased chain-packing compared to APN-SiMe₂OEt (12.5/15.3) Å. This unexpected difference may account for the unique transport properties showing that APN-SiMe₂OEt is a more permeable material than APN-SiMe(OEt)₂.

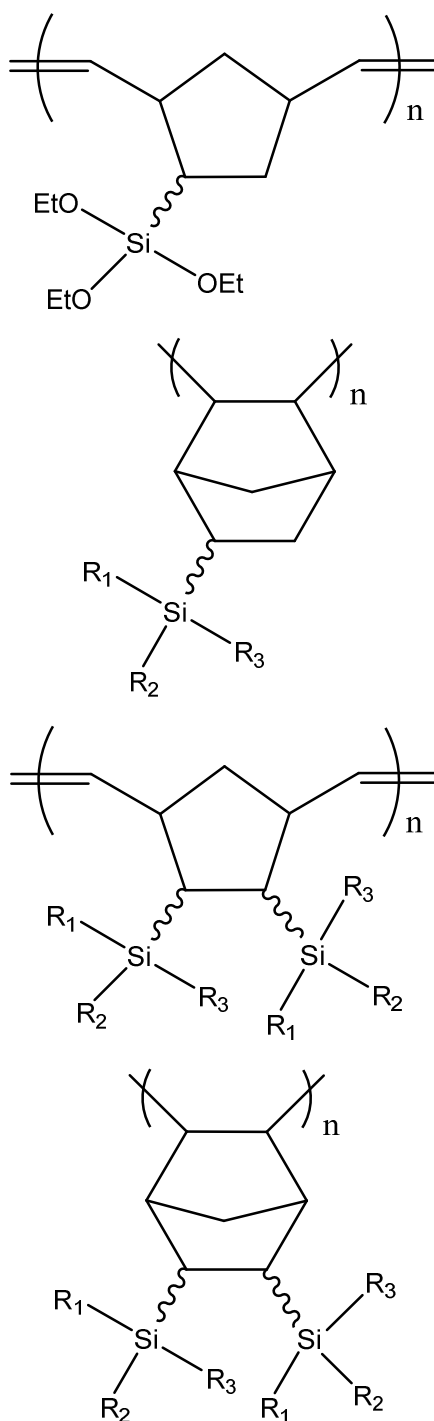
[0058] Two of the polymers, APN-SiMe₂OEt and APN-Si(OEt)₃ also showed a third region of very low scattering angle, which corresponds to very distant interchain packing. These peaks represent spacing as large as (40.9/49.9) Å and may be crucial in retaining high permeabilities at heightened selectivities. One of the polymers, APN-Si(OEt)₃, also showed a fourth peak of very tight interchain packing (4.2/5.1) Å that provides evidence of crosslinking in the addition-polymer with the most ethoxy content. Only one addition-type polymer displays this shift compared to three of the ROMP polymers. The higher glass transitions of the addition-type polymers restricts chain mobility and limit the ability of crosslinking sites to react together when compared with the lower T_g ROMP polymers.

[0059] It should be apparent to those skilled in the art that various modifications and variations can be made to the described embodiments without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various described embodiments provided such modification and variations come within the scope of the appended claims and their equivalents.

CLAIMS

1. A method of making a crosslinked alkoxysilyl polynorbornene homopolymer comprising:
5 polymerizing a norbornene monomer comprising at least one alkoxysilyl moiety in the presence of a catalyst to produce an alkoxysilyl modified polynorbornene homopolymer, and
producing a crosslinked alkoxysilyl polynorbornene homopolymer through sol-gel initiated crosslinking of the alkoxysilyl modified polynorbornene homopolymer at
10 ambient conditions, acid-catalyzed, or base-catalyzed conditions.
2. The method of claim 1, where the polymerizing step comprises an addition polymerization process, which utilizes a transition metal catalyst.
- 15 3. The method of claim 2, where the transition metal catalyst comprises a palladium metallocene derivative catalyst.
4. The method of claim 3, further comprising a trityl borate, a phosphine, or combinations thereof.
20
5. The method of claim 1, where the polymerizing step comprises a ring opening metathesis polymerizing (ROMP) process, which utilizes a Grubbs 1st Generation catalyst, or any later generation of Grubbs catalyst.
- 25 6. The method of claim 1, where the alkoxysilyl moiety includes from one to eighteen alkoxy groups.
7. The method of claim 1, where the crosslinked alkoxysilyl polynorbornene homopolymer has either of the following structures:

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where R₁ is an alkyl, an alkoxy, or alkoxysiloxane, R₂ is an alkyl, an alkoxy, or alkoxysiloxane, R₃ is an alkyl, an alkoxy, or alkoxysiloxane, and n is at least one, where at least one of R₁, R₂, and R₃, is an alkoxy or alkoxysiloxane.

8. The method of claim 7 where at least two of R1, R2, and R3 is an alkoxy or an alkoxysiloxane, where at least two alkoxys are the same or a different moiety.

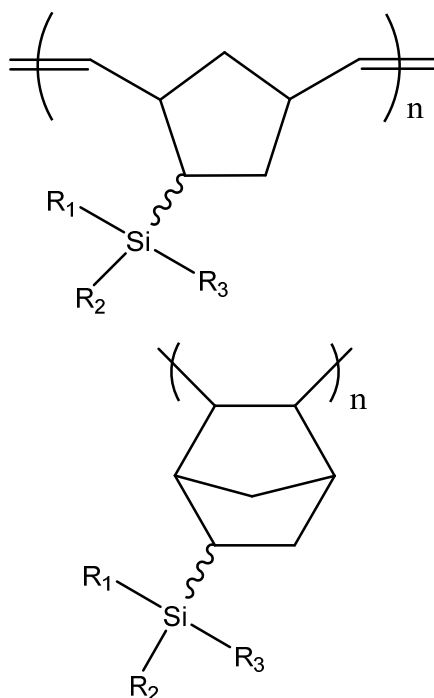
9. The method of claim 1 where the norbornene monomer comprises
 5 methyldiethoxysilylnorbornene, dimethylethoxysilylnorbornene, or triethoxysilylnorbornene.

10. The method claim 1, where the sol-gel initiated crosslinking involves hydrolysis in water or exposure to the atmosphere.
 10

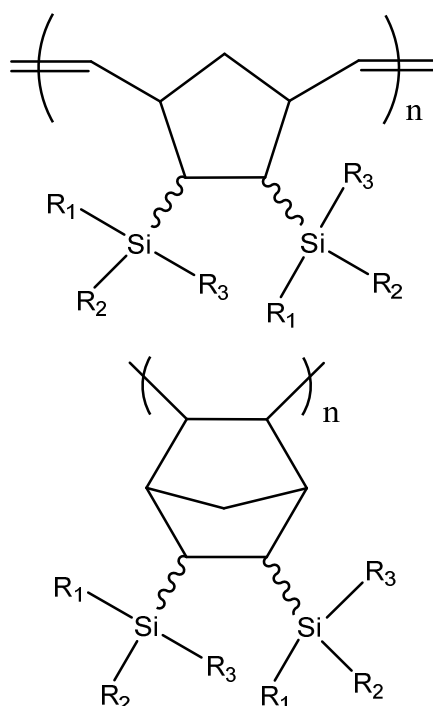
11. The method claim 10, where the sol-gel initiated crosslinking is acid or base catalyzed.

12. The method of claim 1, where the degree of cross-linking is measured by
 15 gel content, and has about 10% to about 100% by weight gel content.

13. A formulation comprising a crosslinked alkoxysilyl polynorbornene homopolymer having either of the following structures:



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where R1 is an alkyl, an alkoxy, or alkoxy-siloxane, R2 is an alkyl, an alkoxy, or alkoxy-siloxane, R3 is an alkyl, an alkoxy, or alkoxy-siloxane, and n is at least one, where
 5 at least one of R1, R2, and R3, is an alkoxy or alkoxy-siloxane; and where the cross-linking is characterized by 10% to 100% by weight gel content.

14. The formulation according to claim 13 where the crosslinked alkoxy-silyl polynorbornene homopolymer includes at least a first chain packing region and a second
 10 chain packing region, where the first chain packing region is defined by a first interchain distance and the second chain packing region is defined by a second interchain distance, the first interchain distance being smaller than the second interchain distance, where the first interchain distance and second interchain distance are
 15 calculated from Bragg's Law for angle peaks measured by Wide Angle X-ray diffraction (WAXRD).

15. The formulation according to claim 14, further comprising a third packing region defined by a third interchain distance, the third interchain distance being larger than the first interchain distance and second interchain distance, where the third
 20 interchain distance is calculated from Bragg's Law for angle peaks measured by WAXRD.

16. The formulation according to claim 15, further comprising a fourth packing region defined by a fourth interchain distance, the fourth interchain distance being smaller than the first, second, and third interchain distances, where the fourth
5 interchain distance is calculated from Bragg's Law for angle peaks measured by WAXRD.

17. The formulation according to claim 13, where the crosslinked alkoxysilyl polynorbornene homopolymer comprises a molecular weight distribution (MWD) from
10 1 to 3, where MWD is defined as M_w/M_n with M_w being a weight average molecular weight and M_n being a number average molecular weight.

18. A natural gas separation membrane comprising the formulation of claim
13.