METHOD OF FABRICATING A CARBON MOLECULAR SIEVE MEMBRANE

Cross-Reference To Related Application

[0001] This application claims the benefit of priority of Singapore patent application No. 201008923-3, filed 3 December 2010, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] Various embodiments relate to a method of fabricating a carbon molecular sieve membrane.

Background

[0003] The implementation of membrane technology for gas separation depends on the integration of membrane material advancement, membrane configuration and module design, and process optimization. Indeed, the development of high performance membrane materials is the vital aspect among these considerations.

[0004] Polymers are attractive candidates for membrane fabrication due to the ease of processability, good physiochemical properties and low production costs. Various polymer design strategies have been explored by membrane scientists in the search of materials with better gas transport properties. The molecular design of polymers, the chemical modification of macromolecules (e.g. cross-linking, sulfonation and ion-exchange) and polymer blending are different synthetic routes that are extensively investigated. A problem associated with the use of glassy polymeric membranes for the separation of condensable gases (e.g. CO_2) is plasticization.

[0005] A typical trade-off relationship exists between gas permeability and permselectivity for most glassy polymers. In other words, an improvement in gas permeability is often accompanied by a reduction in the permselectivity. A feasible approach to circumvent the upper bound and to create a significant enhancement in the

gas separation performance is to transform the organic matrix to highly size-selective inorganic carbon molecular sieve membranes (CMSM). FIG. 1 shows the CO_2/CH_4 separation performance of CMSMs reported in the past decade in comparison to the Robeson's upper bound (Robeson, L. M., J. Membr. Sci. 2008, 320, 390-400).

[0006] Thus, there is a need to provide a carbon molecular sieve membrane with enhanced gas separation performance and anti-plasticization properties and a method of fabricating the carbon molecular sieve membrane.

Summary

[0007] In a first aspect of the invention, a method of fabricating a carbon molecular sieve membrane is provided. The method may include forming a semi-interpenetrating polymer network comprising a linear polymer and a branched polymer, and subjecting the semi-interpenetrating polymer network to a carbonization process.

[0008] In a second aspect of the invention, a carbon molecular sieve membrane is provided. The carbon molecular sieve membrane may be obtainable by the method as described above.

[0009] In a third aspect of the invention, use of a carbon molecular sieve membrane for a gas separation process or a pervaporation process is provided. The carbon molecular sieve membrane may be obtainable by the method as described above.

[0010] In a fourth aspect of the invention, a membrane separator comprising a carbon molecular sieve membrane is provided. The carbon molecular sieve membrane may be obtainable by the method as described above.

[0011] In a fifth aspect of the invention, a semi-interpenetrating polymer network is provided. The semi-interpenetrating polymer network includes a linear polymer and a branched polymer, wherein the linear polymer includes a polyimide and the branched polymer includes an azide.

[0012] In a sixth aspect of the invention, a carbon molecular sieve membrane is provided. The carbon molecular sieve membrane may be obtained by carbonizing the semi-interpenetrating polymer network as described above.

Brief Description of the Drawings

[0013] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the invention are described with reference to the following drawings, in which:

[0014] FIG. 1 shows the CO_2/CH_4 separation performance of polymeric and carbon membranes of the prior art.

[0015] FIG. 2 shows a flow chart illustrating a method of fabricating a carbon molecular sieve membrane, according to various embodiments.

[0016] FIG. 3 shows schematics of a 6FDA-NDA/azide semi-IPN.

[0017] FIG. 4 shows schematics of a 6FDA-TMPDA/azide interconnected semi-IPN.

Detailed Description

[0018] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0019] In the context of various embodiments, the term “about” as applied to a numeric value encompasses the exact value and a variance of +/- 5% of the value.

[0020] Various embodiments provide carbon molecular sieve membranes derived from semi-interpenetrating polymer networks, for applications such as gas separation.

[0021] Various embodiments may provide a method of fabricating carbon molecular sieve membranes (CMSMs), which may potentially be used in gas separation. The

method involves the in-situ formation of semi-interpenetrating polymer networks (semi-IPNs).

[0022] In various embodiments, semi-interpenetrating polymer networks (semi-IPNs) including a linear polymer (e.g. polyimide) and azido-containing monomers (e.g. azides) with multi-reactive sites which may be capable of forming branched polymer networks, are used as precursors for forming the CMSMs. The incorporation of a highly branched polymer network within a linear polymeric matrix may result in better or improved gas separation performance and anti-plasticization properties.

[0023] In the method of fabricating the CMSMs, the semi-interpenetrating polymer networks are subjected to a carbonization process, for example by pyrolysis. In various embodiments, the gas separation performance of the CMSMs may depend on the pyrolysis conditions and/or the chemical compositions of the semi-IPNs.

[0024] As examples and not limitations, a semi-IPN of poly(2,3,5,6-phenylene-2,2'-bis(3,4-carboxylphenyl) hexafluoropropane) diimide (6FDA-TMPDA)/2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (azide) at a ratio of about 90:10 may be formed. Carbonization of the 6FDA-TMPDA/azide semi-IPN may be carried out at a relatively low pyrolysis temperature of about 550°C to form a carbon molecular sieve membrane (CMSM). The CMSM may exhibit a high CO_2 flux of more than about 9000 Barrer and a CO_2/N_2 permselectivity of about 25, and may be used for post-combustion CO_2 capture from flue gas.

[0025] In addition, a semi-IPN of 6FDA-TMPDA/azide at a ratio of about 70:30 may be formed. Carbonization of the 6FDA-TMPDA/azide semi-IPN may be carried out at an elevated pyrolysis temperature of about 800°C to form a carbon molecular sieve membrane (CMSM). The CMSM may exhibit a CO_2/CH_4 selectivity of 170, a CO_2 permeability of about 287 Barrer. In addition, the CMSM exhibits good H_2/CO_2 separation performance, e.g. a H_2 permeability of about 2200 Barrer and a H_2/CO_2 selectivity of 7.7.

[0026] Therefore, by varying the chemical composition of the semi-IPNs and the pyrolysis temperatures, membranes suitable for different applications, for example natural gas sweetening and hydrogen enrichment, may be tailored and formed.

[0027] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of examples and not limitations, and with reference to FIG. 2.

[0028] FIG. 2 shows a flow chart 200 illustrating a method of fabricating a carbon molecular sieve membrane, according to various embodiments.

[0029] At 202, a semi-interpenetrating polymer network comprising a linear polymer and a branched polymer is formed.

[0030] At 204, the semi-interpenetrating polymer network is subjected to a carbonization process. In various embodiments, the carbonization process may be carried out at a temperature between about 550°C and about 800°C, e.g. at about 550°C, at about 600°C, at about 700°C and at about 800°C. The carbonization process may be carried out in a vacuum environment.

[0031] In the context of various embodiments, the term "carbon molecular sieve membrane" may mean an inorganic carbon membrane having pore structures in the molecular size range that may discriminate between molecules on the basis of size (i.e. a porous carbon membrane). Carbon molecular sieve membranes (CMSMs) may provide molecular separations based on the rate of adsorption. CMSMs are non-crystalline or amorphous. In various embodiments, CMSMs may be fabricated via carbonization of a polymeric precursor or precursors, for example by pyrolysis. In various embodiments, where polymeric precursors are carbonized, for example at high temperatures, the mobile polymer chains are transformed to rigid inorganic structure, and the gas transport switches from solution-diffusion to a primarily molecular sieving mechanism.

[0032] In various embodiments, the inorganic CMSMs may be size-selective membranes, and which may circumvent the permeability–permselectivity tradeoff relationship of the conventional membranes and may provide enhanced separation performance. CMSMs may also exhibit enhanced thermal stability and anti-plasticization (or anti-swelling) property.

[0033] In the context of various embodiments, the term "semi-interpenetrating polymer network" or semi-IPN may mean a polymer comprising one or more linear polymers and one or more branched polymers, characterized by the penetration on a molecular scale between the linear polymer(s) and the branched polymer(s). The term as used herein

relates to true semi-IPNs where physical interaction or physical cross-linking between the linear polymer(s) and the branched polymer(s) occurs and the different polymer networks can, in principle, be separated from one another without breaking chemical bonds, as well as cross-linked semi-IPNs where chemical cross-linking between the linear polymer(s) and the branched polymer(s) occurs and separation cannot be done without breaking chemical bonds. Such physical and/or chemical cross-linkings within the semi-IPN may increase the rigidity of the polymer system.

[0034] In various embodiments, a semi-IPN (also known as a pseudo-IPN) may be obtained by the polymerization of the precursors of a branched polymer in the presence of a preformed linear polymer. For example, depending on the functionalities of the host polyimides, chemical cross-links may be formed between the branched azide network and the preformed linear polyimide. The linear component within the semi-IPN may be immobilised via chemical bonds with the networked polymer. This results in interconnected semi-IPNs, where such intralinkages may influence the structural properties of the resultant materials. In various embodiments, the chemical bridges or cross-links in conjunction with the interpenetrating network may restrict the mobility of the polymer chains and may minimise or suppress CO_2-induced plasticization.

[0035] In the context of various embodiments, the term "linear polymer" may mean a polymer composed of linear macromolecules having structures comprising multiple repetition in linear sequence of units derived from molecules of low relative molecular mass.

[0036] In the context of various embodiments, the term "branched polymer" may mean a polymer with at least one branch point intermediate between units. In other words, a branched polymer is composed of a macromolecule with one or more substituent side chains or branches.

[0037] In the context of various embodiments, the term "carbonization" may mean a process by which an organic substance or material is converted into carbon or a carbon-containing residue. In various embodiments, carbonization may be carried out through pyrolysis in an inert atmosphere.

[0038] In the context of various embodiments, the term "pyrolysis" may mean a thermochemical decomposition (i.e. chemical degradation or decomposition caused by

thermal energy or heat) of organic material. In various embodiments, pyrolysis may be performed under vacuum and at elevated temperatures in an environment substantially free of oxygen. In various embodiments, the pyrolysis process involves the elimination of thermally liable functional groups from the organic matrix by means of gas evolution, and the molecular rearrangement of the polymer structure.

[0039] In various embodiments, the branched polymer includes one or more monomers having a plurality of reactive sites for forming the branched polymer. Each monomer may have at least 3 reactive sites, for example 4, 5, 6 or 7 reactive sites. The reactive sites may be functional groups that are the same or different. In various embodiments, at least one of the reactive sites is a functional group that may react with other reactive site(s) on another monomer. As one specific example and not limitation, a monomer may contain two azido (i.e. N_3) groups (azide), two alkene C=C double bonds and one CH_3 group, thus having 5 reactive sites, where the two N_3 groups may react, for example, with the alkene C=C double bond or the C-H bond in CH_3 of another monomer. In addition, molecules or monomers containing other functional groups, for example acrylates, which may form free radicals in the presence of heat or UV may also be used as the branched polymer for forming the polymer network.

[0040] In the context of various embodiments, the term “reactive site” may mean a reactive part of a macromolecule that participate in its specific combination with another molecule.

[0041] In the context of various embodiments, the step of forming the semi-interpenetrating polymer network comprising the linear polymer and the branched polymer comprises polymerizing one or more monomers of the branched polymer in the presence of the linear polymer.

[0042] In various embodiments, the semi-interpenetrating polymer network comprising a linear polymer and a branched polymer may be formed by dissolving the linear polymer in a solvent (e.g. dimethylformamide or dichloromethane) to form a solution, adding the one or more monomers of the branched polymer to the solution to form a mixture solution, casting the mixture solution on a support to form a film or a coating, or spinning the mixture solution to form a hollow fiber membrane, and heating the film or the coating or the hollow fiber membrane.

[0043] In further embodiments, the semi-interpenetrating polymer network comprising a linear polymer and a branched polymer may be formed by dissolving the one or more monomers of the branched polymer in a solvent (e.g. dimethylformamide or dichloromethane) to form a solution, adding the linear polymer to the solution to form a mixture solution, casting the mixture solution on a support to form a film or a coating, or spinning the mixture solution to form a hollow fiber membrane, and heating the film or the coating or the hollow fiber membrane.

[0044] In the context of various embodiments, heating the film or the coating or the hollow fiber membrane may be carried out in a vacuum environment.

[0045] In the context of various embodiments, the semi-interpenetrating polymer network includess the linear polymer and the branched polymer in a ratio of about 90:10 to about 70:30, for example about 90:10, about 85:15, about 80:20, about 75:25 or about 70:30.

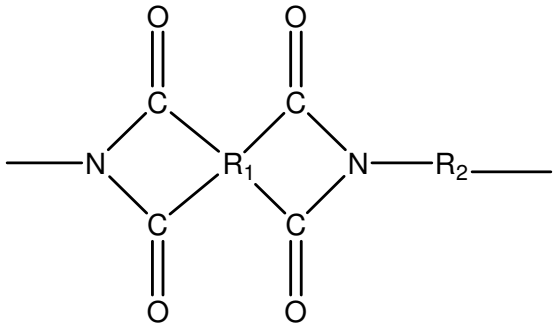
[0046] In various embodiments, the semi-interpenetrating polymer network includes cross-links between the linear polymer and the branched polymer. The cross-links may be chemical and/or physical cross-links.

[0047] In the context of various embodiments, the linear polymer is or includes a polyimide, including but not limited to fluorinated polyimides such as poly(1,5-naphthalene-2,2'-bis(3,4-phthalic) hexafluoropropane) diimide (6FDA-NDA) or poly(2,3,5,6-phenylene-2,2'-bis(3,4-carboxylphenyl) hexafluoropropane) diimide (6FDA-TMPDA), which have high free volume and rigidity. The linear polymer acts as the host polymer. In various embodiments, the polyimide is an aromatic polyimide, i.e. the core moiety of the tetracarboxylic acid anhydride comprises or consists of an aryl moiety, such as phenyl, naphthyl, anthracenyl.

[0048] It should be appreciated that other linear polymers such as poly(ether imide), poly(amide imide), polyamide, poly(ether sulfone), polysulfone, polybenzimidazole, cellulose acetate, poly(phenylene oxide), poly(ether ether ketone) and poly(aryl ether ketone), may also be used.

[0049] In the context of various embodiments, the polyimide has the general chemical structure as shown below, wherein R_1 is the core moiety of the specific tetracarboxylic

acid dianhydride used as an educt, such as, for example C6 aryl, and R_2 is the core moiety of the specific diamine used as an educt, such as, for example 4-phenoxyphenyl.



[0050] It should be appreciated that while any polyimides may be used for forming the pseudo-interpenetrating polymer networks (pseudo-IPNs), polyimides with high intrinsic free volumes and rigidity are preferably used for forming the pseudo-IPNs.

[0051] In the context of various embodiments, a polymer having a high intrinsic free volume may have a fractional free volume of about 0.17 or more (i.e. ≥ 0.17). The fractional free volume (FFV) may be defined as $FFV = (V-V_0)/V$, where V is the specific volume and V_0 is the chain occupied volume. V_0 is about 1.3 times the Van der Waals volume (V_w), where V_w refers to the volume "occupied" by an individual atom (or molecule).

[0052] In various embodiments, the incorporation of a polymer network (i.e. the branched polymer) within the linear polymer may alter the free volume distribution of the resultant semi-IPN. The free volume and its distribution may determine the gas transport property of the semi-IPN and the resultant CMSMs. By providing a linear polymer with a high intrinsic free volume, there is more room or flexibility for altering the free volume distribution of the resultant semi-IPN.

[0053] In the context of various embodiments, the term “free volume” as applied to a polymer may mean the volume of the polymer mass not actually occupied by the molecules themselves. The free volume of the polymer may affect the glass trasition temperature of the polymer.

[0054] In the context of various embodiments, the branched polymer is or includes an azide, including but not limited to 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone, or an acrylate.

[0055] In various embodiments, the linear polymer is or includes a polyimide (e.g. 6FDA-NDA or 6FDA-TMPDA) and the branched polymer is or includes an azide.

[0056] In the context of various embodiments, the azide is used as the cross-linking reagent to form semi-IPNs with the linear polymer (e.g. polyimide). Azide is capable of thermal curing as well as photocuring (e.g. it may react spontaneously in the presence of heat or UV light). In addition to creating cross-linking (e.g. chemical linkages) between the linear polymer chains, azide may also react with itself or its own species to form a network polymer. The network polymer formed by the azide monomer may be termed poly(azide).

[0057] As shown by the chemical structures of 6FDA-NDA and 6FDA-TMPDA below, these polyimides are aromatic polyimides. They have limited chain mobility, which provides rigid frameworks for the polymerization of azide. The firm molecular scaffold may minimize the likelihood of generating a phase-separated semi-IPN, which may be due to a tendency by the branched macromolecule to push apart the existing linear polymer chains when the azide monomers react to form a polymer network.

[0058] In various embodiments, the azido group, N_3 is a linear 1,3-dipolar structure which may form nitrene in the presence of heat or ultraviolet radiation. Nitrenes are highly reactive, short-lived nitrogen intermediates. Nitrenes may be capable of insertion into C-H bonds. For example, the azide may be thermally decomposed such that the thermal decomposition of azide proceeds with an initial rupture of the N≡N bond in the azido-group, thereby releasing nitrogen (N_2) and leaving a highly reactive divalent nitrogen (nitrene). The nitrene group may initiate addition reactions, for example with C–H bonds on the linear polymer/azide structures to form a covalent network.

[0059] The difference between the polyimides 6FDA-NDA and 6FDA-TMPDA is the presence of $-CH_3$ groups in the diamine moieties of 6FDA-TMPDA. 6FDA-NDA does not contain any functional group that may potentially react with azide while 6FDA-TMPDA with the methyl substituent groups ($-CH_3$ groups) may react with azide, where the nitrene radicals may react with the $-CH_3$ groups to form chemical cross-links. Hence, depending on the chemical nature of the host polymer (e.g. the chemical functional groups that are present on the host linear polymer), the combination of polyimide and poly(azide) may result in a semi-IPN or an interconnected (or cross-linked) semi-IPN.

[0060] For example, FIG. 3 shows schematics of a 6FDA-NDA/azide semi-IPN 300 with a host polymide (6FDA-NDA) 302 and a poly(azide) network 304, while FIG. 4 shows schematics of a 6FDA-TMPDA/azide interconnected (or cross-linked) pseudo IPN 400 with a host polymide (6FDA-TMPDA) 402 and a poly(azide) network 404. The host polymide (6FDA-TMPDA) 402 and the poly(azide) network 404 are chemically cross-linked, as represented by 406 to illustrate the cross-links.

[0061] In embodiments where 6FDA-NDA is used as the host polyimide, the azide monomer reacts with its species to form a polymer network which physically interlocks the linear polyimide chains. No chemical bond is formed between the 6FDA-NDA host polymer and the azide polymer network, but physical interactions, thereby forming a true semi-IPN. In various embodiments, the degree of interpeneration between 6FDA-NDA and the poly(azide) increases with increasing azide concentration, for example an increase from about 10 wt% to about 50 wt%.

[0062] In embodiments where 6FDA-TMPDA is used as the host polyimide, one or more of the $–CH_3$ groups of 6FDA-TMPDA may react with the N_3 group present in the azide monomer used for forming the polymer network. Thus, chemical bonds are formed between the 6FDA-TMPDA linear polymer and the azide polymer network, thereby forming a cross-linked semi-IPN.

[0063] In the context of various embodiments, the high free volume of the host linear polyimide may enable modification of the cavity distribution of the resultant composite material upon the formation of the branched poly(azide). The change in the free volume distribution may impact the gas transport properties of the membranes.

[0064] In the context of various embodiments, in order to form a homogenous semi-interpenetrating polymer network, preferably the linear polymers have a high intrinsic chain rigidity. A higher polymer chain rigidity results in a higher glass transition temperature. A higher polymer chain rigidity results in limited chain mobility, which provides rigid frameworks for the polymerization of the monomers (e.g. azide) of the branched polymer. The firm molecular scaffold may minimize the likelihood of generating a phase-separated semi-IPN, which may be due to a tendency by the branched macromolecule to push apart the existing linear polymer chains when the monomers (e.g. azide) react to form a polymer network.

[0065] In the context of various embodiments, a linear polymer having a high intrinsic chain rigidity may have a glass transition temperature, T_g, of about 300°C or more (i.e. $T_g \geq 300°C$).

[0066] In various embodiments, the carbon molecular sieve membrane includes a film membrane or a hollow fiber membrane.

[0067] Various embodiments may also provide a carbon molecular sieve membrane obtainable by the method as described herein. The carbon molecular sieve membrane may be used for a gas separation process or a pervaporation process.

[0068] Various embodiments may also provide a membrane separator comprising a carbon molecular sieve membrane obtainable by the method as described herein. The membrane separator may further include a dehydration unit, for example a glycol dehydration unit.

[0069] Various embodiments may also provide a semi-interpenetrating polymer network. The semi-interpenetrating polymer network may include a linear polymer and a branched polymer, wherein the linear polymer may include a polyimide and the branched polymer may include an azide.

[0070] Various embodiments may also provide a carbon molecular sieve membrane. The carbon molecular sieve membrane may be obtained by carbonizing the semi-interpenetrating polymer network as described above.

Examples

[0071] Various embodiments provide a synthetic method for the preparation of semi-interpenetrating polymer networks (semi-IPNs) and carbon molecular sieve membranes with enhanced gas separation performance and anti-plasticization properties. The method includes the in-situ formation of the semi-IPN including a linear polymer (e.g. a polyimide) and a branched polymer (e.g. azido-containing monomers or azides with multi-reactive sites (or various reactive functional groups)). In other words, for example, the semi-IPN may be formed by the in-situ reaction/polymerization of azide monomers or azido-containing monomers with a plurality of reactive sites within polyimide or the polyimide molecular scaffolds. The azido-containing monomers may form a branched polymer. An example of the azido-containing monomer is 2,6-bis(4-azidobenzylidene)-4-

methylcyclohexanone. Depending on the functional groups present on the linear polymer, cross-links (e.g. chemical cross-links and/or physical cross-links) may be formed between the linear polymer and the branched polymer. In other words, chemical bonds may be formed between the in-situ formed polymer network and the preformed linear polymer, or there may be physical interactions with no chemical bond between the in-situ formed polymer network and the preformed linear polymer.

[0072] The in situ polymerization of azide within the rigid polyimide frameworks creates homogeneous semi-IPNs with enhanced gas transport properties. The incorporation and polymerization of azide within the host polyimide allows manipulation of the cavity size and free volume distribution.

[0073] The carbon molecular sieve membranes formed may be used in various applications, including but not limited to membrane gas separation and pervaporation applications. The following non-limiting examples illustrate the method according to various embodiments.

[0074] Example 1: Fabrication of 6FDA-NDA/azide semi-IPN dense film.

[0075] The monomers 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (also known as 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride) and 1,5-naphthalenediamine (NDA) were first sublimated under vacuum. Subsequently, 6FDA–NDA was synthesized via the chemical imidization approach.

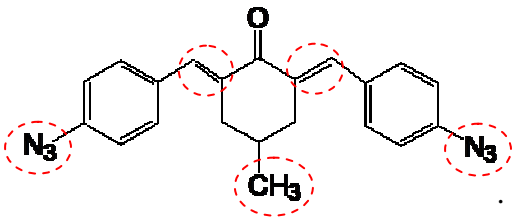
[0076] N-methyl-2-pyrrolidone (NMP) was first purified by vacuum distillation. Equimolar amounts of dianhydride and diamines were dissolved in NMP under nitrogen atmosphere to form a viscous solution of poly(amic acid). The reaction between the dianhydride and diamine is spontaneous and may not require the addition of initiator. The total solid concentration was about 20% by weight. 3-picoline and acetic anhydride (molar ratio of about 1:4) were added to form the polyimide. 3-picoline serves as the catalyst for the polycondensation reaction while acetic anhydride is the dehydrating agent. The polyimide solution was then precipitated in methanol and dried under vacuum at about 120°C.

[0077] As an example and not limitations, the polymerization reaction for forming the linear polyimide may be as follows. Stoichiometric amount of diamine was dissolved in

NMP, and then stoichiometric amount of dianhydride was added to the diamine/NMP solution. The dianhydride/diamine/NMP solution was then stirred at ambient temperature (e.g. about 25ºC) until the solution became viscous, which indicated the formation of poly(amic acid). 3-picoline and acetic anhydride were added to form the polyimide. The polyimide solution was then precipitated in methanol and washed with fresh methanol twice to remove unreacted monomers. The polyimide polymer was dried in an oven under vacuum at about 120 ºC. The polyimide polymer may then be used for membrane fabrication.

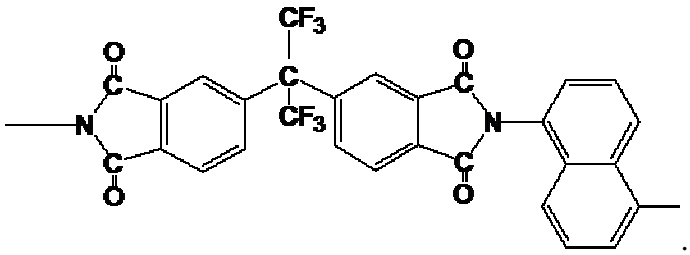
[0078] In order to prepare a film casting or mixture solution, the azide monomer (2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone) was first dissolved in dimethylformamide (DMF) and stirred for about 1 hour. Subsequently, the 6FDA-NDA polymer (poly(1,5-naphthalene-2,2'-bis(3,4-phthalic) hexafluoropropane) diimide) was added to the solution and stirred overnight to form the mixture solution. The polymer concentration in the solvent was about 5 wt.% while the azide loading in the polymer was varied from 0 to about 30 wt.%. In various embodiments, the polymerization reaction of the azide branched polymer may be initiated by heat or UV. As an example and not limitations, the polymerization reaction may take place, with heat as the initiator, during the heat treatment of the polymer film as described below. The reaction may occur at about 150ºC.

[0079] The chemical structure of 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (azide) is



[0080] The azide has 5 reactive sites, as indicated by the dashed circles in the chemical structure above.

[0081] The chemical structure of poly(1,5-naphthalene-2,2'-bis(3,4-phthalic) hexafluoropropane) diimide (6FDA-NDA) is



[0082] Table 1 shows the chemical compositions of the respective casting solution prepared, which are also the chemical compositions of the respective semi-IPN.

[0083] Table 1: Mass compositions of the polyimide/azide casting solutions.

Polyimide/azide composition (wt%:wt%)	Mass of polyimide (g)	Mass of solvent (g)	Mass of azide (g)
100:0	1.149	21.83	0
90:10	1.149	21.83	0.128
70:30	1.149	21.83	0.492

[0084] The casting or mixture solution was filtered using a 1.0 μm polytetrafluoroethylene (PTFE) membrane before ring casting onto a silicon (Si) wafer plate at about 55°C to form a film or a coating. After about 5 days, most of the solvent has evaporated, leaving behind a nascent film. The nascent film was then heat treated or annealed in vacuum, by maintaining a temperature of about 60°C for about 24 hours, increasing the temperature to about 250°C at a rate of about 12°C/20 minutes, maintaining the temperature of about 250°C for about 24 hours and followed by natural cooling to room temperature (e.g. about 25°C), to form 6FDA-NDA and 6FDA-NDA/azide membranes. The thicknesses of the polymeric membranes were about 50 ± 5 μm. The membranes were homogenous and dense. During the heat treatment process of the film or coating, polymerization reaction of the azido-containing monomers may take place, for example at about 150ºC.

[0085] It should be appreciated that the mixture solution may also be spun to form hollow fiber membranes, e.g. asymmetric hollow fiber membranes.

[0086] The pure gas transport properties of the 6FDA-NDA and the 6FDA-NDA/azide semi-IPN membranes were obtained using a constant volume-variable pressure gas

permeation chamber. The gas permeability and ideal permselectivity are shown in Tables 2 and 3, respectively.

[0087] Table 2: Pure gas permeability of 6FDA-NDA and 6FDA-NDA/azide membranes.

Sample	**Permeability (Barrer)**			
	H_2	**N_2**	**CH_4**	**CO_2**
6FDA-NDA	77.6	1.74	1.02	38.0
6FDA-NDA/azide (90:10)	38.6	0.54	0.26	12.9
6FDA-NDA/azide (70:30)	26.0	0.28	0.14	6.61

[0088] The measurements for the gas permeability for N_2, CH_4 and CO_2 were performed at a temperature of about 35°C and a pressure of about 10 atm (standard atmosphere). The measurement for the gas permeability for H_2 was performed at a temperature of about 35°C and a pressure of about 3.5 atm.

[0089] The Barrer is a unit for gas permeability, where 1 Barrer is equivalent to about 1×10^{-10} cm^3 (STP)-cm/(cm^2 s cmHg) or about 7.5005×10^{-18} m^2 s^{-1} Pa^{-1}. The term "STP" refers to standard temperature and pressure.

[0090] Table 3 : Ideal permselectivity of 6FDA-NDA and 6FDA-NDA/azide membranes.

Sample	**Permselectivity**			
	CO_2/CH_4	**CO_2/N_2**	**H_2/N_2**	**H_2/CO_2**
6FDA-NDA	37.4	21.8	44.6	1.82
6FDA-NDA/azide (90:10)	49.5	23.9	71.6	2.63
6FDA-NDA/azide (70:30)	47.2	23.6	92.9	3.35

[0091] The permselectivity for different pairs of gases as shown in Table 3 were calculated from the respective gas permeability as shown in Table 2.

[0092] As shown in Table 2, as the azide content increases, the gas permeability decreases. As shown in Table 3, incorporation of a small amount of azide (e.g. about 10 wt%) increases the CO_2/CH_4 selectivity. A further increase in the azide, for example to about 30 wt%, leads to further reduction in the gas permeability with no corresponding increase in the selectivity.

[0093] As shown in Table 3, the incorporation of azide within the linear 6FDA-NDA polyimide shows negligible effect on the CO_2/N_2 selectivity, but leads to an increase in the respective selectivity for H_2/N_2 and H_2/CO_2.

[0094] In addition, CO_2/CH_4 binary gas tests were conducted for the 6FDA-NDA/azide (90:10) membrane and the results (Table 4) show that there is no or minimal plasticizing effect, even at high CO_2 partial pressures.

[0095] Table 4 : CO_2/CH_4 separation performance obtained from binary gas tests at 35°C for 6FDA-NDA and 6FDA-NDA/azide (90:10) membranes.

Sample	**Binary CO_2/CH_4 (90:10) at 10 atm**		**Binary CO_2/CH_4 (90:10) at 20 atm**		**Binary CO_2/CH_4 (90:10) at 30 atm**	
	P_{CO_2} (Barrer)	**α_{CO_2/CH_4}**	**P_{CO_2} (Barrer)**	**α_{CO_2/CH_4}**	**P_{CO_2} (Barrer)**	**α_{CO_2/CH_4}**
6FDA-NDA	25.8	45.9	25.8	41.8	26.0	32.2
6FDA-NDA/azide (90:10)	18.2	56.5	16.2	47.1	12.0	37.1

[0096] As shown in Table 4, the results obtained from the mixed gas tests are in line with the pure gas tests (Tables 2 and 3), illustrating that the addition of azide improves the CO_2/CH_4 separation performance or permselectivity. In addition, the CO_2 permeability and CO_2/CH_4 selectivity of 6FDA-NDA/azide (90:10) decrease as the pressure increases. This may be attributed to the saturation of CO_2 sorption sites at higher pressures.

[0097] Example 2: Fabrication of cross-linked 6FDA-TMPDA/azide semi-IPN.

[0098] The monomer 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (also known as 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride) was first sublimated under vacuum. The monomer 2,3,5,6-Tetramethyl-1,4-phenylenediamine (TMPDA) was purified by recrystallization in methanol at about 55°C. Subsequently, 6FDA–TMPDA was synthesized via the chemical imidization approach.

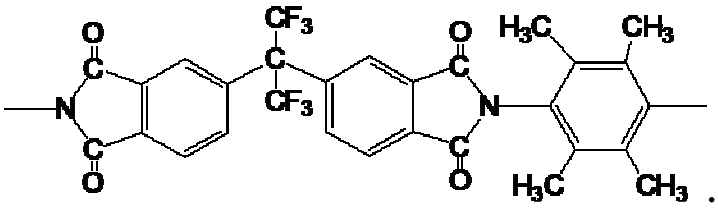
[0099] N-methyl-2-pyrrolidone (NMP) was first purified by vacuum distillation. Equimolar amounts of dianhydride and diamines were dissolved in NMP under nitrogen

atmosphere to form a viscous solution of poly(amic acid). The reaction between the dianhydride and diamine is spontaneous and may not require the addition of initiator. The total solid concentration was about 20% by weight. 3-picoline and acetic anhydride (molar ratio of about 1:4) were added to form the polyimide. 3-picoline serves as the catalyst for the polycondensation reaction while acetic anhydride is the dehydrating agent. The polyimide solution was then precipitated in methanol and dried under vacuum at about 120°C.

[0100] As an example and not limitations, the polymerization reaction for forming the linear polyimide may be as follows. Stoichiometric amount of diamine was dissolved in NMP, and then stoichiometric amount of dianhydride was added to the diamine/NMP solution. The dianhydride/diamine/NMP solution was then stirred at ambient temperature (e.g. about 25ºC) until the solution became viscous, which indicated the formation of poly(amic acid). 3-picoline and acetic anhydride were added to form the polyimide. The polyimide solution was then precipitated in methanol and washed with fresh methanol twice to remove unreacted monomers. The polyimide polymer was dried in an oven under vacuum at about 120 ºC. The polyimide polymer may then be used for membrane fabrication.

[0101] In order to prepare a film casting or mixture solution, the azide monomer (2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone) was first dissolved in dichloromethane (DCM) and stirred for about 1 hour to form the mixture solution. Subsequently, the 6FDA-TMPDA polymer (poly(2,3,5,6-tetramethyl-1,4-phenylene-2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane) diimide) was added to the solution and stirred overnight. The polymer concentration in the solvent was about 5 wt.% while the azide loading in the polymer was varied from 0 to about 30 wt.%. In various embodiments, the polymerization reaction of the azide branched polymer may be initiated by heat or UV. As an example and not limitations, the polymerization reaction may take place, with heat as the initiator, during the heat treatment of the polymer film as described below. The reaction may occur at about 150ºC.

[0102] The chemical structure of poly(2,3,5,6-tetramethyl-1,4-phenylene-2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane) diimide (6FDA-TMPDA) is



[0103] The chemical compositions of the respective casting solution prepared, which are also the chemical compositions of the respective semi-IPNs, are similar to that shown in Table 1.

[0104] The casting or mixture solution was filtered using a 1.0 μm PTFE membrane before ring casting onto a silicon (Si) wafer plate at about 25°C to form a film or a coating. The casting temperature was different from that for the fabrication of 6FDA-NDA/azide semi-IPN (Example 1) as the casting temperature depends on the volatility of the solvent and to allow slow solvent evaporation for forming the polymer film. After about 5 days, most of the solvent has evaporated, leaving behind a nascent film. The nascent film was then heat treated or annealed in vacuum, by maintaining a temperature of about 60°C for about 24 hours, increasing the temperature to about 250°C at a rate of about 12°C/20 minutes, maintaining the temperature of about 250°C for about 24 hours and followed by natural cooling to room temperature (e.g. about 25°C), to form 6FDA-TMPDA and 6FDA-TMPDA/azide membranes. The thicknesses of the polymeric membranes were about 50 ± 5 μm. The membranes were homogenous and dense. During the heat treatment process of the film or coating, polymerization reaction of the azido-containing monomers may take place, for example at about 150ºC.

[0105] It should be appreciated that the mixture solution may also be spun to form hollow fiber membranes, e.g. asymmetric hollow fiber membranes.

[0106] The pure gas transport properties of the 6FDA-TMPDA and the 6FDA-TMPDA/azide semi-IPN membranes were obtained using a constant volume-variable pressure gas permeation chamber. The gas permeability and ideal permselectivity are shown in Tables 5 and 6, respectively.

[0107] Table 5: Pure gas permeability of 6FDA-TMPDA and 6FDA-TMPDA/azide membranes.

Sample	Permeability (Barrer)			
	H_2	N_2	CH_4	CO_2
6FDA-TMPDA	358	19.4	15.5	315
6FDA-TMPDA/azide (90:10)	186	7.12	5.29	133
6FDA-TMPDA/azide (70:30)	86.1	1.97	1.22	38.6

[0108] The measurements for the gas permeability for N_2, CH_4 and CO_2 were performed at a temperature of about 35°C and a pressure of about 10 atm. The measurement for the gas permeability for H_2 was performed at a temperature of about 35°C and a pressure of about 3.5 atm.

[0109] Table 6 : Ideal permselectivity of 6FDA-TMPDA and 6FDA-TMPDA/azide membranes.

Sample	Permselectivity			
	CO_2/CH_4	CO_2/N_2	H_2/N_2	H_2/CO_2
6FDA-TMPDA	20.3	16.2	18.5	1.00
6FDA-TMPDA/azide (90:10)	25.1	18.6	26.1	1.20
6FDA-TMPDA/azide (70:30)	31.6	19.6	43.7	1.95

[0110] The permselectivity for different pairs of gases as shown in Table 6 were calculated from the respective gas permeability as shown in Table 5.

[0111] As 6FDA-TMPDA contains methyl substituent groups, chemical cross-links are formed between the linear polyimide and the azide network.

[0112] As shown in Table 5, as the azide content increases, the gas permeability, including CO_2 permeability, decreases. As shown in Table 6, as the azide content increases, the permselectivity, including CO_2/CH_4 selectivity, increases.

[0113] In addition, CO_2/CH_4 binary gas tests were conducted and the results (Table 7) show that the presence of the azide network effectively suppresses CO_2-induced plasticization.

[0114] Table 7 : CO_2/CH_4 separation performance obtained from binary gas tests at 35°C for 6FDA-TMPDA and 6FDA-TMPDA/azide (70:30) membranes.

Sample	Binary CO_2/CH_4 (90:10) at 10 atm		Binary CO_2/CH_4 (90:10) at 20 atm		Binary CO_2/CH_4 (90:10) at 30 atm	
	P_{CO_2} (Barrer)	α_{CO_2/CH_4}	P_{CO_2} (Barrer)	α_{CO_2/CH_4}	P_{CO_2} (Barrer)	α_{CO_2/CH_4}
6FDA-TMPDA	246	24.8	254	18.1	276	9.3
6FDA-TMPDA/azide (70:30)	37.1	32.1	31.7	26.8	28.9	25.4

[0115] As shown in Table 7, the results obtained from the mixed gas tests are in line with the pure gas tests (Tables 5 and 6), illustrating that the addition of azide improves the CO_2/CH_4 separation performance or permselectivity. In addition, the CO_2 permeability and CO_2/CH_4 selectivity of 6FDA-TMPDA/azide (70:30) decrease as the pressure increases. This may be attributed to the saturation of CO_2 sorption sites at higher pressures.

[0116] In various embodiments, the good CO_2/CH_4 selectivity and improved anti-plasticization properties of the semi-IPNs or semi-IPN membranes are obtained at the expense of reduced gas permeability. In order to obtain membranes with high selectivity and permeability, pyrolysis of the semi-IPN membranes were performed, thereby forming carbon molecular sieve membranes (CMSMs) derived from the semi-IPNs. The CMSMs formed may be used for various applications, including gas separation.

[0117] Example 3: Carbonization of cross-linked 6FDA-TMPDA/azide semi-IPNs.

[0118] The 6FDA-TMPDA and the 6FDA-TMPDA/azide dense membranes were used as the precursors for forming the CMSMs. Pyrolysis was performed using a Lenton high vacuum ($<1 \times 10^{-5}$ torr) tube furnace (Model VTF12). The polymeric precursors were placed on a wire mesh during the heat treatment or pyrolysis process.

[0119] The heat treatment protocol for the carbonization of the 6FDA-TMPDA and the 6FDA-TMPDA/azide dense membranes in a vacuum environment was carried out by maintaining a temperature of about 50°C for about 30 minutes, increasing the temperature to about 400°C at a rate of about 3°C/minute, increasing the temperature to about 550°C at a rate of about 1°C/minute, maintaining the temperature of about 550°C for about 1 hour and followed by natural cooling to room temperature (e.g. about 25°C), to form the CMSMs.

[0120] The pure gas transport properties of the 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs were obtained using a constant volume-variable pressure gas permeation chamber. The gas permeability and ideal permselectivity are shown in Tables 8 and 9, respectively.

[0121] Table 8: Pure gas permeability of 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs carbonized at about 550°C.

Sample	**Permeability (Barrer)**			
	H_2	**N_2**	**CH_4**	**CO_2**
6FDA-TMPDA	16024	277	116	6937
6FDA-TMPDA/azide (90:10)	12190	373	307	9460
6FDA-TMPDA/azide (70:30)	9556	151	56.0	3360

[0122] The measurements for the gas permeability for N_2, CH_4 and CO_2 were performed at a temperature of about 35°C and a pressure of about 10 atm. The measurement for the gas permeability for H_2 was performed at a temperature of about 35°C and a pressure of about 3.5 atm.

[0123] Table 9 : Ideal permselectivity of 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs carbonized at about 550°C.

Sample	**Permselectivity**			
	CO_2/CH_4	**CO_2/N_2**	**H_2/N_2**	**H_2/CO_2**
6FDA-TMPDA	59.8	25.3	57.8	2.31
6FDA-TMPDA/azide (90:10)	30.8	25.3	32.7	1.29
6FDA-TMPDA/azide (70:30)	60.0	22.3	56.9	2.84

[0124] The permselectivity for different pairs of gases as shown in Table 9 were calculated from the respective gas permeability as shown in Table 8.

[0125] As shown in Tables 8 and 9, the 6FDA-TMPDA/azide (90:10) CMSM carbonized at about 550°C exhibits a high CO_2 permeability or flux of greater than 9000 Barrer and a CO_2/N_2 selectivity of about 25. In applications for post-combustion CO_2 capture from flue gas (which contains nitrogen, carbon dioxide (CO_2), sulfur oxides and water vapor), membranes with a high flux is desirable, due to the large volumetric flux of the flue gas. Therefore, the 6FDA-TMPDA/azide (90:10) CMSM may be used in CO_2/N_2 separation.

[0126] In addition, as shown in Tables 8 and 9, the 6FDA-TMPDA CMSM carbonized at about 550°C exhibits a high CO_2 permeability or flux of about 7000 Barrer and a CO_2/CH_4 selectivity of about 60. This membrane may be applied in the treatment of natural gas streams.

[0127] Example 4: Carbonization of cross-linked 6FDA-TMPDA/azide semi-IPNs.

[0128] The 6FDA-TMPDA and the 6FDA-TMPDA/azide dense membranes were used as the precursors for forming the CMSMs. Pyrolysis was performed using a Lenton high vacuum ($<1 \times 10^{-5}$ torr) tube furnace (Model VTF12). The polymeric precursors were placed on a wire mesh during the heat treatment or pyrolysis process.

[0129] The heat treatment protocol for the carbonization of the 6FDA-TMPDA and the 6FDA-TMPDA/azide dense membranes in a vacuum environment was carried out by maintaining a temperature of about 50°C for about 30 minutes, increasing the temperature to about 400°C at a rate of about 3°C/minute, increasing the temperature to about 800°C at a rate of about 1°C/minute, maintaining the temperature of about 800°C for about 1 hour and followed by natural cooling to room temperature (e.g. about 25°C), to form the CMSMs.

[0130] In various embodiments, the final pyrolysis temperature used to fabricate the CMSMs may alter the gas transport properties of the resultant CMSMs.

[0131] The pure gas transport properties of the 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs were obtained using a constant volume-variable pressure gas permeation chamber. The gas permeability and ideal permselectivity are shown in Tables 10 and 11, respectively.

[0132] Table 10: Pure gas permeability of 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs carbonized at about 800°C.

Sample	Permeability (Barrer)			
	H_2	N_2	CH_4	CO_2
6FDA-TMPDA	5622	60.8	25.9	1900
6FDA-TMPDA/azide (90:10)	3470	27.9	10.3	837
6FDA-TMPDA/azide (70:30)	2201	9.04	1.69	287

[0133] The measurements for the gas permeability for N_2, CH_4 and CO_2 were performed at a temperature of about 35°C and a pressure of about 10 atm. The measurement for the gas permeability for H_2 was performed at a temperature of about 35°C and a pressure of about 3.5 atm.

[0134] Table 11 : Ideal permselectivity of 6FDA-TMPDA and 6FDA-TMPDA/azide CMSMs carbonized at about 800°C.

Sample	Permselectivity			
	CO_2/CH_4	CO_2/N_2	H_2/N_2	H_2/CO_2
6FDA-TMPDA	73.5	31.2	92.4	2.96
6FDA-TMPDA/azide (90:10)	81.0	30.0	125	4.15
6FDA-TMPDA/azide (70:30)	170	31.8	243	7.67

[0135] The permselectivity for different pairs of gases as shown in Table 11 were calculated from the respective gas permeability as shown in Table 10.

[0136] As shown in Table 11, the 6FDA-TMPDA/azide CMSMs obtained by carbonization at about 800°C exhibits good CO_2/CH_4 and H_2/CO_2 separation performances. For example, for the 6FDA-TMPDA/azide (70:30) membrane, a CO_2/CH_4 selectivity of about 170 may be obtained. Moreover, the same membrane displays a H_2/CO_2 selectivity of about 7.7 and a high H_2 permeability of about 2200 Barrer, as shown in Tables 10 and 11.

[0137] Various embodiments provide a method of fabricating semi-interpenetrating polymer networks (semi-IPNs), for example of a linear polymer and a branched polymer, for forming membrane materials. The method is an in-situ approach and is an

improvement over the simple physical blending approach. The method enables the forming of homogenous membranes. In various embodiments, the physical and/or chemical cross-links or interconnections within the semi-IPN may suppress CO_2-induced plasticization, which is a common problem encountered in the use of glassy polymeric membranes for gas separation.

[0138] In various embodiments, the semi-IPNs or semi-IPN membranes formed may be subjected to a carbonization process, by pyrolysis, to form carbon molecular sieve membranes (CMSMs). In various embodiments, the chemical compositions of the semi-IPNs and/or the pyrolysis conditions (e.g. temperatuure) may be varied or changed to modify or alter the properties (e.g. gas transport properties) of the CMSMs. Various embodiments of the CMSMs derived from the semi-IPNs show recommendable gas separation performance.

[0139] Various embodiments of the CMSMs prepared or fabricated at a pyrolysis temperature of about 550°C exhibit high gas permeability. This property or characteristic makes the CMSMs suitable for use in post combustion CO_2 capture from flue gas, e.g.. CO_2/N_2 separation., as membranes with high CO_2 permeability and CO_2/N_2 selectivity in the range of between about 20 and 40 are suitable for use in post-combustion CO_2 capture.

[0140] Various embodiments of the CMSMs prepared or fabricated at a pyrolysis temperature of about 800°C exhibit high permselectivity, in particular for CO_2/CH_4 separation. The CMSMs may be used for natural gas purifications.

[0141] Furthermore, as shown in Table 11, the CMSM of the 6FDA-TMPDA/azide (70:30) membrane obtained after being carbonized at about 800°C exhibits recommendable H_2/CO_2 separation performance, and therefore may be applied to syngas purification.

[0142] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method of fabricating a carbon molecular sieve membrane, the method comprising:

forming a semi-interpenetrating polymer network comprising a linear polymer and a branched polymer; and

subjecting the semi-interpenetrating polymer network to a carbonization process.

2. The method as claimed in claim 1, wherein the branched polymer comprises one or more monomers comprising a plurality of reactive sites for forming the branched polymer.

3. The method as claimed in claim 2, wherein the step of forming the semi-interpenetrating polymer network comprising the linear polymer and the branched polymer comprises:

polymerizing one or more monomers of the branched polymer in the presence of the linear polymer.

4. The method as claimed in claim 1, wherein the semi-interpenetrating polymer network comprises the linear polymer and the branched polymer in a ratio of about 90:10 to about 70:30.

5. The method as claimed in claim 1, wherein the linear polymer is selected from the group consisting of polyimide, poly(ether imide), poly(amide imide), polyamide, poly(ether sulfone), polysulfone, polybenzimidazole, cellulose acetate, poly(phenylene oxide), poly(ether ether ketone) and poly(aryl ether ketone).

6. The method as claimed in claim 1, wherein the branched polymer comprises an azide or an acrylate.

7. The method as claimed in claim 1, wherein the linear polymer comprises a polyimide and the branched polymer comprises an azide.

8. The method as claimed in claim 7, wherein the polyimide comprises poly(1,5-naphthalene-2,2'-bis(3,4-phthalic) hexafluoropropane) diimide (6FDA-NDA) or poly(2,3,5,6-phenylene-2,2'-bis(3,4-carboxylphenyl) hexafluoropropane) diimide (6FDA-TMPDA).

9. A semi-interpenetrating polymer network comprising a linear polymer and a branched polymer, wherein the linear polymer comprises a polyimide and the branched polymer comprises an azide.

10. A carbon molecular sieve membrane obtained by carbonizing the semi-interpenetrating polymer network of claim 9.