

CROSS-LINKED POLYMER, MEMBRANE AND PROCESSES OF FORMING THE SAME

TECHNICAL FIELD

5 **[0001]** The present invention refers to a process for making a cross-linked polymer, to a membrane comprising the cross-linked polymer made by the process and use of the membrane in separation process.

BACKGROUND

10 **[0002]** Extensive research has been carried out on development of membranes with advanced or novel functions for separation processes, such as ultrafiltration, gas separation, reverse osmosis, and pervaporation, as it has many advantages such as appreciable energy savings, clean technology with ease of operation and flexibility in system design, when compared to other conventional separation techniques such as distillation, ion-exchange and chemical treatment.

15 **[0003]** There are a variety of methods for fabricating a wide range of membranes. Various groups have produced membranes using novel processing technologies of polymers for membranes, such as synthesis of novel polymers with well-defined structure, advanced membrane surface functionalization, use of templates to create tailored barrier or surface structures for membranes, and preparation of composite membranes with synergistic
20 combination of the functions of individual components.

25 **[0004]** In particular, demands of pharmaceutical industry have provided the impetus to develop enantioselective membranes suitable for chiral separation, as majority of the active pharmaceutical ingredients are chiral in nature. Chiral chemicals, otherwise known as enantiomers, have the same chemical structure but are mirror images of each other. As a result, they may possess different biological properties and efficacies. Use of an isomer with a different chirality can result in adverse or even fatal consequences. In time to come, enantiomerically pure drug compounds could be one of the criteria for active pharmaceutical ingredients to be accepted by the US Food and Drug Administration (FDA). Therefore, research on chiral separation has received worldwide attention. Traditional methods to isolate
30 the desired enantiomer are asymmetric synthesis, preferential crystallization, chromatography, and capillary electrophoresis. There continues to be a need for new technologies to lower production costs, increase product purity, and overcome limitations of batch processes.

[0005] It is therefore an object of the present invention to provide a process for making

polymers, to develop novel membrane materials which can be used in separation processes that overcome, or at least ameliorate, one or more of the disadvantages described above.

SUMMARY OF THE INVENTION

[0006] In a first aspect, the present invention provides a process for making a cross-linked polymer. The process comprises exposing a polymer to a cross-linking agent. The cross-linking agent includes at least one cyclodextrin moiety. The cyclodextrin moiety carries at least one reactive group. The process also includes exposing the polymer to the cross-linking agent under conditions so as to form a cross-linked polymer via the reactive group. As a result, a cross-linked polymer is formed.

[0007] In a second aspect, the invention provides a process for making a cross-linked polymer. The process comprises providing a membrane which is present in solid form. The membrane is exposed to a cross-linking agent. The cross-linking agent includes at least one cyclodextrin moiety. The cyclodextrin moiety carries at least one reactive group. The process also includes exposing the polymer to the cross-linking agent under conditions so as to form a cross-linked polymer via the reactive group. As a result, a cross-linked polymer is formed.

[0008] In a third aspect, the invention provides a cross-linked polymer. The cross-linked polymer is obtainable by the process of the first and/or second aspect.

[0009] In a fourth aspect, the invention relates to the use of a cross-linked polymer in the formation of a membrane. The cross-linked polymer is a cross-linked polymer according to the third aspect.

[0010] In a fifth aspect, the invention relates to the use of a membrane in separation processes. The membrane is a membrane according to the fourth aspect.

[0011] The invention will be better understood with reference to the detailed description when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] **Fig. 1A** is a field emission scanning electron microscopy (FESEM) picture of neat MATRIMID® membrane. **Fig. 1B** is a field emission scanning electron microscopy (FESEM) picture of MATRIMID®/ β -cyclodextrin membrane with 5 wt% β -cyclodextrin. The membrane was modified with β -cyclodextrin through physical mixing. **Fig. 1C** is a field emission scanning electron microscopy (FESEM) picture of MATRIMID®/ β -cyclodextrin membrane with 5 wt% β -cyclodextrin. The membrane was modified by β -cyclodextrin through cross-linking. It can be seen that phase inversion phenomenon is present in membrane formed from

Matrimid® which is physically mixed with β -CD in Fig. 1B, and which is not observed with membrane formed from cross-linked Matrimid® shown in Fig. 1C.

[0013] Fig. 2 is a graph showing thermogravimetric analysis (TGA) characterization curves of neat poly(amide imide) (PAI) membrane, poly(amide imide) (PAI-CD) membrane cross-linked with m-xylenediamine- β -cyclodextrin (XDA- β -CD), and m-xylenediamine- β -cyclodextrin (XDA- β -CD). Mass of XDA- β -CD grafted on the membranes can be derived from the TGA curves.

[0014] Fig. 3 is a graph showing estimated amount of cyclodextrin per unit surface area of cross-linked PAI-CD membrane under various modification times. The amount of cyclodextrin per unit surface area increases with modification time until a modification time of about 1 hour. Subsequently, a decrease in amount of cyclodextrin was observed with further increase in modification time.

DETAILED DESCRIPTION OF THE INVENTION

[0015] In a first aspect, the present invention provides a process for making a cross-linked polymer. The process comprises exposing a polymer to a cross-linking agent. The cross-linking agent includes at least one cyclodextrin moiety. The cyclodextrin moiety carries at least one reactive group. The process also includes exposing the polymer to the cross-linking agent under conditions so as to form a cross-linked polymer via the reactive group. As a result, a cross-linked polymer is formed.

[0016] The use of a cross-linking agent of a cyclodextrin moiety results in chemical durability and anti-swelling properties for the resultant polymer, due to interaction between the polymer and reactive group on the cross-linking agent, which prevents dissolution of the cyclodextrin moiety into the reaction solution. In addition, because of the cross-linking between cross-linking agent and polymer, swelling of the polymer is counteracted. The cyclodextrin moiety also provides enhanced separation efficiency due to its molecular discrimination properties.

[0017] The term “cross-link” as used herein refers to an interconnection between polymer chains. The term “cross-linking agent” refers to an agent which induces cross-linking. The cross-linking agent has at least one cyclodextrin moiety. The cyclodextrin moiety may be either of α -, β - or γ - form, which contains six, seven or eight glucopyranose units respectively. Alternatively, it can be macrocycle of oligosaccharides containing more than eight glucopyranose units. Examples of cyclodextrins moieties that are suitable include, but are not limited to, α -cyclodextrin, β -cyclodextrin, γ -cyclodextrin, dimethyl- α -cyclodextrin, trimethyl-

α -cyclodextrin, dimethyl- β -cyclodextrin, trimethyl- β -cyclodextrin, dimethyl- γ -cyclodextrin, and trimethyl- γ -cyclodextrin.

[0018] The cyclodextrin moiety has at least one reactive group. The term "reactive group" as used herein refers to a chemical moiety which exhibits bond formation capability. The reactive group can be covalently bonded to the cyclodextrin moiety. The reactive group may be bonded to any position on the cyclodextrin moiety. The number of reactive groups may be one or more, i.e. 1, 2, 3, 4, 5, 6 or more. The reactive group may be any functional group that can react with polymers to form covalent bonding. The reactive group can be any group that bears functionality of monomer, i.e. any such desired group that can be polymerized. When the number of reactive groups is two or more, the reactive groups can be identical or different. The usability of each group may depend on several conditions, for example the respective applications and the reaction conditions, and can be determined empirically. Examples of a suitable reactive group include, but are not limited to, an amino group, a hydroxyl group, an allyl glycidyl group, an epoxide group, a thiol group, an oxetane group, a C=C group, an allyl group, an allyl glycidyl ether group, a C $\equiv$ C group, or substituted derivatives thereof. Non limiting examples of suitable C=C groups may be acrylic and methacrylic amides, acrylic and methacrylic esters, vinyl or acetylene moieties or a butadiene moiety.

[0019] In one embodiment, the cyclodextrin moiety is diamine modified cyclodextrin having the general Formula 1:



wherein X is a cyclodextrin moiety and R is a hydrocarbon. The hydrocarbon may be an aliphatic, alicyclic or aromatic hydrocarbon.

[0020] The term "aliphatic" means, unless otherwise stated, a straight or branched hydrocarbon chain, which may be saturated or mono- or poly-unsaturated and include heteroatoms. An unsaturated aliphatic group contains one or more double and/or triple bonds (alkenyl or alkynyl moieties). The branches of the hydrocarbon chain may include linear chains as well as non-aromatic cyclic elements. The hydrocarbon chain, which may, unless otherwise stated, be of any length, and contain any number of branches. Typically, the hydrocarbon (main) chain includes 0 to 3, to 6, to 8, to 12, to 15 or to 18 carbon atoms. Examples of alkenyl radicals are straight-chain or branched hydrocarbon radicals which contain one or more double bonds. Alkenyl radicals generally contain about two to about eighteen carbon atoms and one or more, for instance two, double bonds, such as about two to about ten carbon atoms, and one double bond. Alkynyl radicals normally contain about two to about eighteen carbon atoms and

one or more, for example two, triple bonds, preferably such as two to ten carbon atoms, and one triple bond. Examples of alkynyl radicals are straight-chain or branched hydrocarbon radicals which contain one or more triple bonds. Examples of alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, the n isomers of these radicals, isopropyl, isobutyl, isopentyl, sec-butyl, tert-butyl, neopentyl, 3,3 dimethylbutyl. Both the main chain as well as the branches may furthermore contain heteroatoms as for instance N, O, S, Se or Si or carbon atoms may be replaced by these heteroatoms.

[0021] The term "alicyclic" means, unless otherwise stated, a non-aromatic cyclic moiety (e.g. hydrocarbon moiety), which may be saturated or mono- or poly-unsaturated. The cyclic hydrocarbon moiety may also include fused cyclic ring systems such as decalin and may also be substituted with non-aromatic cyclic as well as chain elements. The main chain of the cyclic hydrocarbon moiety may, unless otherwise stated, be of any length and contain any number of non-aromatic cyclic and chain elements. Typically, the hydrocarbon (main) chain includes 3, 4, 5, 6, 7 or 8 main chain atoms in one cycle. Examples of such moieties include, but are not limited to, cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl. Both the cyclic hydrocarbon moiety and, if present, any cyclic and chain substituents may furthermore contain heteroatoms, as for instance N, O, S, Se or Si, or a carbon atom may be replaced by these heteroatoms. The term "alicyclic" also includes cycloalkenyl moieties which are unsaturated cyclic hydrocarbons, which generally contain about three to about eight ring carbon atoms, for example five or six ring carbon atoms. Cycloalkenyl radicals typically have a double bond in the respective ring system. Cycloalkenyl radicals may in turn be substituted. Examples of such moieties include, but are not limited to, cyclohexenyl, cyclooctenyl or cyclodecenyl.

[0022] The term "aromatic" means, unless otherwise stated, a planar cyclic hydrocarbon moiety of conjugated double bonds, which may be a single ring or include multiple fused or covalently linked rings, for example, 2, 3 or 4 fused rings. The term aromatic also includes alkylaryl. Typically, the hydrocarbon (main) chain includes 5, 6, 7 or 8 main chain atoms in one cycle. Examples of such moieties include, but are not limited to, cyclopentadienyl, phenyl, or naphthalenyl. An example of an alkylaryl moiety is benzyl. The main chain of the cyclic hydrocarbon moiety may, unless otherwise stated, be of any length and contain any number of heteroatoms, as for instance N, O and S. Examples of such heteroaromatic moieties (which are known to the person skilled in the art) include, but are not limited to, furanyl-, thiophenyl-, or naphthyl-. By the term "arylaliphatic" is meant a hydrocarbon moiety, in which one or more aromatic moieties are substituted with one or more aliphatic groups. Thus the term "arylaliphatic" also includes hydrocarbon moieties, in which two or more aryl groups are connected via one or more aliphatic chain or chains of any length, for instance a methylene

group. Typically, the hydrocarbon (main) chain includes 5, 6, 7 or 8 main chain atoms in each ring of the aromatic moiety. Examples of arylaliphatic moieties such as alkylaryl moieties include, but are not limited, to 1-ethyl-naphthalene, 1,1'-methylenebis-benzene, or 9-isopropylantracene.

5 [0023] Examples of diamines that can be used to modify cyclodextrin include, but are not limited to, ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylenetetramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, a
 10 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2,2-dimethylpropylenediamine, N-methyl-bis(3-aminopropyl)amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis (3-aminopropyl) sulphide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 2,β-diaminotoluene, m-xylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl- 4, 6-diethyl-1, 3-phenylene-diamine, benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 1,5-diaminonaphthalene, bis (4-aminophenyl) methane, bis (2-chloro-4-amino-3, 5-diethylphenyl) methane, bis (4- aminophenyl) propane, 2, 4-bis (b-amino-t-butyl) toluene, bis (p-b-amino-t-butylphenyl) ether, bis (p-b-methyl-o- aminophenyl) benzene, bis (p-b-methyl-o-aminopentyl) benzene, 1,3-diamino-4-isopropylbenzene, bis (4- aminophenyl) sulphide, bis (4-aminophenyl) sulfone, bis(4-aminophenyl) ether, 1,3-bis(3-aminopropyl) tetramethyldisiloxane, and mixtures thereof.

[0024] Suitable amine functional groups for modifying cyclodextrin for the present invention
 25 include primary amine groups. Specific examples of aliphatic amine groups include, but are not limited to, methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, cyclohexylamine, dimethylamine, diethylamine, dipropylamine, diisopropylamine, ethylene diamine, and mixtures thereof. Specific examples of aliphatic aromatic amine groups include, but are not limited to, meta-xylylenediamine, para-xylylenediamine, and mixtures thereof.

[0025] In one illustrative embodiment, ethylenediamine-β-cyclodextrin is used (see also Example 1). In another illustrative embodiment, m-xylenediamine-β-cyclodextrin is used (see also Example 2).

[0026] In principle, all types of polymer that can be made into membranes by common

techniques such as non-solvent induced phase inversion can be used. Phase inversion is a term used to describe the physical phenomena by which a polymer dissolved in a continuous phase solvent system inverts into a solid macromolecular network in which the polymer is the continuous phase. This event can be induced through several means: removal of solvent (e.g.,
5 evaporation; also known as dry process), addition of another species, addition of a non-solvent or addition to a non-solvent (also known as wet process). In a non-solvent induced phase inversion method, the polymer solution can be poured or extruded into a non-solvent bath. The process can proceed in the following manner. The polymer solution undergoes a transition from a single phase homogeneous solution to an unstable two phase mixture: polymer rich and
10 polymer poor fractions. Micellar droplets of non-solvent in the polymer rich phase can serve as nucleation sites and become coated with polymer. At a critical concentration of polymer, the droplets can precipitate from solution and solidify. Given favorable surface energy, viscosity and polymer concentrations, the micelles can coalesce and precipitate to form a continuous polymer network.

15 **[0027]** A respective polymer may for example be a homopolymer or a copolymer. The polymer may in some embodiments be a linear, i.e. straight, polymer. In some embodiments it may be a hyperbranched polymer. Generally, the polymer can be selected to have a molecular weight in the range from about 500 - 1000 000, including from about 500 - 500 000, 500 - 200 000, 500 - 100 000, 500 - 50 000, 500 - 25 000, 500 - 10 000 or 500 - 5000. Examples of
20 polymers include, but are not limited to, optionally substituted polyamide, optionally substituted polyimide, polyamide-imide, polyetherimide, polycarbonate, polysulfone, polyethersulfone, polyester, polyurethane, polyetherketone, poly(phenylene oxide), cellulose acetate, cellulose triacetate, rubbery polymer, vinyl polymer, polymer/inorganic filler mixed matrix material, copolymer and mixtures thereof.

25 **[0028]** In one embodiment of the present invention, the polymer is a polyimide. It can be a polyimide having a similar structure as that of MATRIMID®. In another embodiment, the polymer is a poly(amide imide). It can be a poly(amide imide) having a similar structure as that of TORLON®.

30 **[0029]** The polymer and/or cross-linking agent can be provided in a suitable solvent. The polymer and/or cross-linking agent may also be dissolved in a suitable solvent. Methods such as mechanical stirring, heating and ultrasonic mixing may be used to aid in dissolving. The solvent can be an organic solvent such as ketone, for example acetone, or a polar solvent such as water, or any solvent that is suitable for dissolving the polymer and/or cross-linking agent, such as alcohols, acetic acid, acetone, formamide, tetrahydrofuran, methyl ethyl ketone, ethyl

acetate, acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide, hexane, benzene, diethyl ether, diethylene glycol dimethyl ether, methylene chloride, carbon tetrachloride, trichloroethylene, N-methyl pyrrolidinone, and mixtures thereof.

[0030] In one illustrative embodiment, N-methyl pyrrolidinone is used (see also Example 3).

5 In another illustrative embodiment, water is used (see also Example 4).

[0031] Typically, amount of cyclodextrin in the cross-linked polymer is selected to have a weight percentage in the range of about 0.01 wt% to about 50 wt%, about 0.01 wt% to about 30 wt%, about 0.01 wt% to about 15 wt%, or about 0.01 wt% to about 5 wt% of the combined amount of cyclodextrin and polymer. A person skilled in the art is able to choose and
10 determine the appropriate quantities of starting materials to derive a desired weight percentage of cyclodextrin in the cross-linked polymer.

[0032] For example, the amount of polymer and cross-linking agent in the solution can be expressed as a weight percentage of polymer and cross-linking agent to the combined amount of solvent, polymer and cross-linking agent. Any suitable weight ratio can be used as long as it
15 does not interfere with the cross-linking of the polymer. For example, the combined amount of polymer and cross-linking agent in the solution can be selected to have a weight percentage in the range from about 1 wt% to about 20 wt %, about 1 wt% to about 15 wt%, about 1 wt% to about 10 wt%, about 1 wt% to about 5 wt%, about 5 wt% to about 20 wt%, about 10 wt% to about 20 wt%, or about 15 wt% to about 20 wt% of the combined amount of solvent, polymer
20 and cross-linking agent.

[0033] The amount of polymer in the solution can also be expressed as a weight ratio with the cross-linking agent. For example, for a neat polymer in which amount of cross-linking agent is 0, the weight ratio of polymer to cross-linking agent in the solution is 100 to 0. Typically, the weight ratio of polymer to cross-linking agent in the solution is selected to be about 98 to
25 about 2, about 95 to about 5, about 90 to about 10, about 85 to about 15, or about 80 to about 20. The amount of polymer in the solution can also be expressed as a mole ratio of the polymer repeat unit with the cross-linking agent. For example, in one embodiment at which MATRIMID® is used as the polymer and ethylenediamine- β -cyclodextrin is used as the cross-linking agent, the mole ratio of polymer repeat unit to cross-linking agent in the solution is
30 about 42 to about 1. This amounts to about 2 wt% (weight percentage expressed in terms of the combined amount of cyclodextrin and polymer) of cyclodextrin in the cross-linked polymer. As a further example, for about 5 wt% of cyclodextrin in cross-linked polymer, in which MATRIMID® is used as the polymer, mole ratio of polymer repeat unit to cross-linking agent in the solution is about 35 to about 1. Both the weight ratio of polymer to cross-linking
35 agent and mole ratio of polymer repeat unit to cross-linking agent can depend on several

conditions, for example the type of polymer and the extent of specific cross-linking, and can be determined empirically.

[0034] Generally, the pH of the solution at which reaction is carried out can be in any range. It can take place in the range of between about 2 to about 13, or between about 2 to about 7, or between about 7 to about 13.

[0035] The exposing step is preferably undertaken at a temperature below the boiling point of the solvent. The temperature undertaken for the exposing step will be dependent on the type and amount of solvent, polymer and cross-linking agent used. The exposing step may be undertaken at a temperature in the range from about 0°C to about 100°C, including from about 20°C to about 100°C, about 30°C to about 100°C, about 40°C to about 100°C, and about 50°C to about 100°C, 0°C to about 90°C, 0°C to about 80°C, 0°C to about 70°C, 0°C to about 60°C, and 0°C to about 50°C.

[0036] The time undertaken for the exposing step will be dependent on the concentration of the cross-linking agent in solution, the temperature of the solution and degree of cross-linking desired. The exposing step may be undertaken for a time period in the range from about 3 seconds to about 24 hours, including from about 60 seconds to about 24 hours, about 5 minutes to about 24 hours, about 1 hour to about 24 hours, about 2 hours to about 24 hours, about 6 hours to about 24 hours, about 12 hours to about 24 hours, and about 18 hours to about 24 hours.

[0037] In one illustrative embodiment, the exposing step is carried out at a temperature of about 50°C for 24 hours.

[0038] In a second aspect, the invention provides a process for making a cross-linked polymer. The process comprises providing a polymer which is present in solid form. The polymer can, for example, be in the form of a membrane, a sheet, rod, tube or molded article. The polymer is exposed to a cross-linking agent. The cross-linking agent includes at least one cyclodextrin moiety. The cyclodextrin moiety carries at least one reactive group. The process also includes exposing the polymer to the cross-linking agent under conditions so as to form a cross-linked polymer via the reactive group. As a result, a cross-linked polymer is formed.

[0039] The membrane may be neat or modified. The membrane may be in the form of a flat sheet, a dense film, asymmetric film, asymmetric hollow fiber, dual layer hollow fiber, composite membrane, or any form suitable for use in fluid separation systems or fluid/particle separation systems. The membrane can be exposed to the cross-linking agent by immersing the membrane in a solution containing the cross-linking agent over a suitable amount of time. The amount of cross-linking agent in the solution and the exposure time can be determined

empirically by determining the degree of cross-linking. The degree of cross-linking can, for example be determined by methods well known in the art such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC) of the so prepared membranes (see, for instance Example 7 of the experimental section or also, for instance, Lee et al., Preparation and characterization of proton-conducting crosslinked diblock copolymer membranes, Journal of Applied Polymer Science, Volume 107 Issue 2, Pages 819 – 824 (2007); Rhim et al., Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group: proton and methanol transport through membranes, Journal of Membrane Science, Volume 238, Issue 1-2, Pages 143-151 (2004)). As shown in the Example section, depending on the exposure time and concentration of the cross-linking agent, a reaction equilibrium may be reached in the cross-linking reaction, wherein a maximum degree of reaction is achieved at a certain reaction period.

[0040] In one embodiment, cross-linking agent m-xylenediamine- β -cyclodextrin is dissolved in water to form a 2 mmol solution.

[0041] In a third aspect, the invention provides a cross-linked polymer. The cross-linked polymer is formed by exposing a polymer to a cross-linking agent. The cross-linking agent includes at least one cyclodextrin moiety. The cyclodextrin moiety carries at least one reactive group. The process also includes exposing the polymer to the cross-linking agent under conditions so as to form a cross-linked polymer via the reactive group. As a result, a cross-linked polymer is formed.

[0042] In one embodiment, the cross-linked polymer is formed from cross-linking reaction between polymer MATRIMID® and ethylenediamine- β -cyclodextrin. In another embodiment, the cross-linked polymer is formed from cross-linking reaction between polymer TORLON® and m-xylenediamine- β -cyclodextrin.

[0043] In a fourth aspect, the invention accordingly also provides a membrane formed from a cross-linked polymer as described above. The membrane may be formed from any method, such as, but not limited to, film casting, extrusion or melt blowing.

[0044] In one embodiment, the membrane is formed by film casting method. The cross-linked polymer may be provided in a solvent to form a casting solution. The solvent may be N-methyl-2-pyrrolidone. The casting solution is degassed to suppress cavitation. The degassing step may be carried out by leaving the casting solution to stand at room temperature and pressure for a period of time, or it may be carried out under vacuum. The time period required for degassing is dependent on the quantity of casting solution and concentration of cross-linked polymer in the solvent. The casting solution may then be cast by conventional

techniques into thin films, beads, fibers, and hollow fibers. In the case of films, a spreader knife over a glass plate or other smooth surface such as Teflon™ at an ambient temperature and pressure may be used to prepare films. Following the casting step, the membrane may be air-dried at room temperature or may be dried at an elevated temperature in a furnace under vacuum. The drying step may be undertaken for a time period in the range from about 3 seconds to about 36 hours, including from about 60 seconds to about 36 hours, about 30 minutes to about 36 hours, about 1 hour to about 36 hours, about 2 hours to about 36 hours, about 6 hours to about 36 hours, about 12 hours to about 36 hours, and about 18 hours to about 36 hours. The drying step may be undertaken at a temperature in the range from about 25°C to about 200°C, including from about 50°C to about 200°C, about 100°C to about 200°C, about 150°C to about 200°C, about 25°C to about 150°C, and about 25°C to about 100°C

[0045] In a fifth aspect, the invention relates to the use of a membrane as described above in separation processes. Examples of separation systems include, but are not limited to, filtration, micro-filtration, nano-filtration, ultra-filtration, gas separation, pervaporation water treatment, and reverse osmosis. The membrane may, for example, be suitable for biofuels purification, separation of isomers, such as structural isomers and stereoisomers and pharmaceutical chiral separation, separation of fluid mixtures, and separating particles from fluids.

[0046] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0047] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

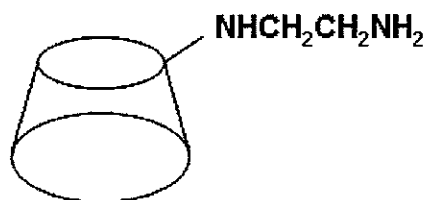
[0048] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

- 5 [0049] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples. It is understood that modification of detail may be made without departing from the scope of the invention.

EXAMPLES

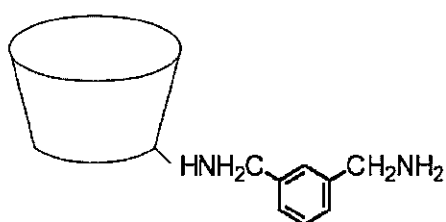
10 Example 1: Synthesis of cross-linking agent ethylenediamine- β -cyclodextrin

- [0050] 5 g of 6-o-monotosyl- β -cyclodextrin (Mono-6-OTs- β -CD) was heated to 75°C and an excess amount (30 ml) of ethylenediamine (EDA) was added. After 4 hours, the reaction was completed and the mixture was allowed to cool to room temperature. 30 ml of cold acetone was added to precipitate the EDA- β -CD produced. Since the precipitated EDA- β -CD formed a suspension in the solvent/non-solvent mixture, a centrifuge operating at 20,000 rpm was used to separate EDA- β -CD from the liquid. Subsequently, acetone was drained off from the centrifuge, and the precipitates were dissolved in a 30 ml water-methanol mixture. The precipitation and dissolution procedure was repeated several times to remove residual EDA. The sample separated in the last cycle of wash was dried at 50°C for 3 days in vacuum.
- 20 Ethylenediamine- β -cyclodextrin formed has a chemical structure as shown:



25 Example 2: Synthesis of cross-linking agent m-xylenediamine- β -cyclodextrin

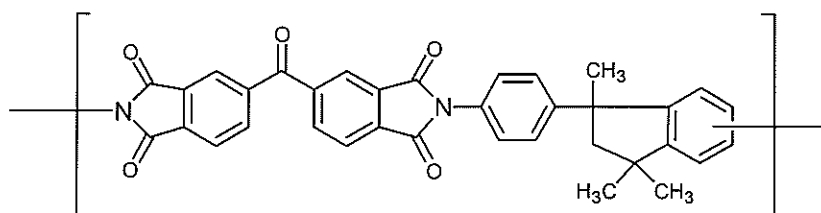
- [0051] 5 g of 6-o-p-toluenesulphonyl- β -cyclodextrin was added to an excess amount (30 ml) of m-xylene diamine (XDA) and stirred for about 4 hours at 75 °C for 4 hours to form m-xylenediamine- β -cyclodextrin (XDA- β -CD), having a chemical structure as shown:



After reaction was completed, the mixture was allowed to cool to room temperature. 30 ml of cold acetone was added to precipitate the XDA- β -CD produced. Since the precipitated XDA- β -CD formed the suspension in the solvent/non-solvent mixture, a centrifuge operating at 20,000 rpm was used to separate the XDA- β -CD from the liquid. Thereafter, the acetone was drained off and the precipitates were dissolved in a 30 ml water/methanol mixture present in a 1:1 weight ratio. The precipitation and dissolution procedure was repeated several times to remove residual XDA. The sample separated in the last cycle of wash was dried at 50 °C for 3 days in vacuum, and XDA- β -CD was obtained with yield of about 20 to about 80 wt%. The yield of XDA- β -CD obtained can be dependent on parameters such as number of times at which the precipitation and dissolution cycle is repeated and the volume of solvent used. The number of polyamine group covalently bonded to one cyclodextrin molecule can be increased if more reaction sites on the cyclodextrin are activated.

Example 3: General procedure for treatment of polymer with cross-linking agent

[0052] 0.019 g of ethylenediamine- β -cyclodextrin was added to 12.4 g of solvent n-methylpyrrolidinone and stirred using magnetic stirrer for about 24 hours at room temperature. Subsequently, 0.97 g of a polyimide material, MATRIMID®, having a chemical structure as shown:



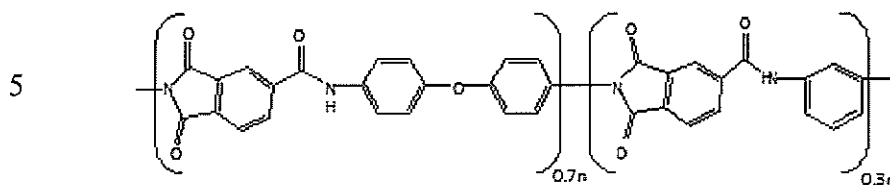
was added to the mixture and stirred for about 24 hours. The amount of cyclodextrin, polymer and solvent are based on the final polymer/cyclodextrin concentration in solvent and the ratio of polymer to cyclodextrin.

[0053] The mixture was then degassed under vacuum for about 4 hours, after which it was cast on a glass plate using a casting knife to form a membrane with about 2 wt% of cyclodextrin loading in polymer matrix. The membrane was put into a vacuum oven at 100 °C for about 30 minutes. Subsequently, it was allowed to cool before it was peeled from the glass plate and put between two wire meshes.

[0054] The membrane was then put back into the furnace where it was maintained at a temperature of 100 °C - 200 °C for about 36 hours, after which the membrane were cooled to room temperature and then removed from the furnace.

Example 4: Synthesis of neat membrane and subsequent treatment with cross-linking agent

[0055] TORLON®, having a chemical structure below:



was added to a solvent n-methyl-pyrrolidinone (NMP) and stirred for about 24 hours. The amount of TORLON® used was 28 wt% of the NMP solution. The mixture was then degassed under vacuum for 4 hours, after which the mixture was cast on a glass plate using a casting knife to form a neat asymmetric membrane. The neat asymmetric membrane was put into a vacuum oven at 100 °C for about 30 minutes. Subsequently, the neat asymmetric membrane was allowed to cool before it was peeled from the glass plate and put between two wire mesh.

[0056] The neat asymmetric membrane was then put back into the furnace where it was maintained at a temperature of about 100 °C – 200 °C for about 36 hours, after which the neat asymmetric membrane was cooled to room temperature and then removed from the furnace.

[0057] m-xylenediamine-β-cyclodextrin was added to water at 50 °C to form a 2 mmol solution. The neat asymmetric membrane was immersed in the m-xylenediamine-β-cyclodextrin cross-linking solution for cross-linking reaction to occur between the membranes and the cross-linking agent. Through variation of the reaction temperature and time, the grafting amount of cyclodextrin and degree of cross-linking can be controlled.

Example 5: Pervaporation cell experimental set-up

[0058] A static pervaporation cell and a commercialized Sulzer Pervaporation System were used to test membrane performance at room temperature. A testing membrane was placed in the stainless steel permeation cell with an effective surface area of 15.2 cm². The system was stabilized for 2 hours before collection of samples. Thereafter, permeate samples were collected by a cold trap immersed in liquid nitrogen at 1 hour interval for 5 hours. The samples were weighted by a Mettler Toledo balance. The sample compositions were analyzed with three parallel injections by a Hewlett-Packard GC 6890 with a HP-INNOWAX column (packed with cross-linked polyethylene glycol) and a thermal conductivity detector (TCD). Finally, the data of flux and composition were averaged. The feed content varied less than 1 wt% during the entire experiment and can be therefore considered as constant during the experiment because of the large quantity of feed solution comparing to the permeate sample.

[0059] There are two factors that determine the performance of a pervaporation system; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor. Productivity is expressed as a parameter called flux (expressed by the unit $l/m^2 \cdot h$). Selectivity and productivity are membrane-dependent.

5 [0060] Flux and separation factors can be calculated by the following equations:

$$J = \frac{Q}{At} \quad \text{Equation (1)}$$

$$\alpha_{2/1} = \frac{y_2 / y_1}{x_2 / x_1} \quad \text{Equation (2)}$$

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wherein, J is flux, Q is total mass transferred over time t (hour), A is the membrane area (m^2), α is separation factor of membrane for Component 2 to Component 1, x_2 and y_2 are the weight or mole fractions of Component 2 in the feed and permeate, respectively, and x_1 and y_1 are the weight or mole fractions of Component 1 in the feed and permeate, respectively.

15 [0061] Driving force for pervaporation can be expressed as vapor pressure difference between components on both sides of the membrane. In most previous researches, membrane flux defined by Equation (1) was used to characterize the membrane productivity. For dense membrane, flux is additionally dependent on thickness of membrane. Therefore, to allow for a more meaningful and accurate comparison of membrane performance, thickness-normalized
20 flux is used which can be calculated using Equation (3):

$$\text{Normalized flux} = \text{Flux (J)} \times \text{membrane thickness (l)} \quad \text{Equation (3)}$$

wherein, J is the flux defined in Equation (1) and l is membrane thickness in μm .

Example 6: Characterisation of polymer membranes

Isopropanol dehydration properties of cross-linked MATRIMID® membranes

25 [0062] Table 1 shows isopropanol dehydration properties in terms of flux of penetrant normalised by membrane thickness (units in $g/m^2 \cdot hr$) and separation factor of neat MATRIMID membrane®, MATRIMID® membranes modified by physical mixing of cyclodextrin at 2 wt%, 5 wt%, 10 wt% and 20 wt% (denoted as β -CD, wt % in parenthesis) and cross-linked MATRIMID® membranes at 2 wt%, 5 wt% and 10 wt% (denoted as N- β -
30 CD, wt % in parenthesis). The weight percentages denoted are expressed with respect to total weight of the membrane.

Table 1

Membrane		Flux (g/m ² -hr)		Separation factor
No.	Description	Water	Isopropanol	
1	Neat MATRIMID®	1,165	4.68	1,623
2	MATRIMID ®/ β -CD (2)	1,482	2.97	3,252
3	MATRIMID ®/ β -CD (5)	1,618	1.62	6,512
4	MATRIMID ®/ β -CD (10)	1,567	0.4704	21,722
5	MATRIMID ®/ β -CD (20)	933	92.34	65.9
6	MATRIMID ®/N- β -CD (2)	845	0.846	6,137
7	MATRIMID ®/N- β -CD (5)	1,056	0.422	15,351
8	MATRIMID ®/N- β -CD (10)	1,603	2.89	3,406

[0063] From Table 1, results obtained demonstrate that MATRIMID® membranes generally show an improvement in separation factor upon addition of cyclodextrin up to a certain cyclodextrin loading after which membrane performance deteriorates. For MATRIMID® membranes modified by physical mixing, membranes containing up to 10 wt% cyclodextrin demonstrated an increase in performance. For cross-linked MATRIMID® membranes, membranes containing up to 5 wt% cyclodextrin demonstrated an increase in performance. Membrane 5, which was modified by physical mixing of cyclodextrin at 20 wt%, however, showed a decrease in separation factor, which could be caused by phase separation of cyclodextrin as a result of its high loading in the membrane. This leads to poorer membrane performance. When comparing between membranes of equivalent weight % of cyclodextrin obtained using the two methods, there is an improvement of separation factor for cross-linked membranes at 2 wt% (1.9 times) and 5 wt% (2.4 times) cyclodextrin loading. Membrane 8, which was cross-linked with 10 wt% of cyclodextrin, shows a decrease in performance compared to the membrane physically mixed with an equivalent amount of β -CD. One possible reason is that with the high amount of cross-linked cyclodextrin, covalent bonding between cyclodextrin and MATRIMID® interferes with MATRIMID® chain packing.

Field Emission Scanning Electron Microscopy (FESEM) pictures of cross-linked MATRIMID® membranes

[0064] Figures 1 A, B and C show the FESEM pictures of neat Matrimid® membranes and Matrimid®/cyclodextrin composite membranes. From the figures, it can be seen that phase inversion phenomenon is present in Matrimid®/ β -CD membrane modified by physical mixing as shown in Figure 1B, and which is not observed with Matrimid®/N- β -CD formed from cross-linking reaction shown in Figure 1C. This means that the membrane as formed by one embodiment of the present invention provides a membrane that does not phase separate, which

is one of the problems encountered by membranes which are modified by physical mixing.

Butanol isomer separation properties of cross-linked TORLON® membranes

[0065] An experiment was carried out to investigate butanol isomer separation properties of cross-linked TORLON® membrane, in both asymmetric and dense form, compared to neat TORLON® and dense TORLON® membrane modified with an equivalent amount of cyclodextrin by physical mixing. Table 2 shows the butanol isomer separation properties in terms of flux of penetrant (units in $\text{g/m}^2\text{-hr}$) and separation factor of neat TORLON® membrane, TORLON® dense membrane modified by cyclodextrin by physical mixing, cross-linked TORLON® asymmetric membrane and cross-linked TORLON® dense membrane.

Table 2

Membrane		Flux ($\text{g/m}^2\text{-hr}$)		Separation factor
No.	Description	n-butanol	t-butanol	
9	Neat Torlon	2.79	2.49	1.11
10	Torlon/ β -CD dense membrane (physical mixing)	3.86	3.11	1.24
11	Torlon asymmetric membrane modified by m-XDA- β -CD water solution	7.62	4.88	1.56
12	Torlon dense membrane modified by m-XDA- β -CD water solution	1.88	0.82	2.30

[0066] From Table 2, results obtained demonstrate that TORLON® membranes show an improvement in separation factor upon addition of cyclodextrin. When comparing between dense membranes of equivalent weight % of cyclodextrin obtained using the two methods, there is an improvement of separation factor of 1.9 times. The dense membrane after surface modification with this cyclodextrin derivative shows depressed flux compared to the neat membrane. However, by applying surface modification on asymmetric membranes, enhanced permeation flux is obtained.

Example 7: Thermogravimetric analysis (TGA) of membranes

[0067] Thermogravimetric analysis was used to characterize neat poly(amide imide) (PAI) membrane and cross-linked poly(amide imide) (PAI-CD) membranes. The cross-linked PAI-CD membranes were modified using m-xylenediamine- β -cyclodextrin (XDA- β -CD) under various exposure times. Figure 2 is a graph showing TGA characterization curves of neat poly(amide imide) (PAI) membrane, cross-linked poly(amide imide) (PAI-CD) membrane and m-xylenediamine- β -cyclodextrin (XDA- β -CD). The TGA curve of neat PAI membrane shows an almost negligible weight loss of about 0.50 wt% during this temperature range. The TGA curve of pure XDA- β -CD shows a main weight loss of about 56 wt% between the temperature

range of 240 to 360 °C. Likewise, the grafted XDA-β-CD on the cross-linked PAI-CD membrane decomposes during this temperature range, and the weight loss reflects mass of XDA-β-CD grafted on the membrane.

[0068] The relationship can be expressed using Equation (4) as follows:

$$\Delta m_{\text{total}} = (m_{\text{total}} - m_{\text{CD}}) \times G_{\text{membr}} + m_{\text{CD}} \times G_{\text{CD}} \quad \text{Equation (4)}$$

wherein Δm_{total} is the total weight loss obtained from the TGA curve; m_{total} and m_{CD} refers to the total membrane weight and weight of grafted cyclodextrin on the membrane surface respectively; G_{membr} and G_{CD} are the weight loss percentages of neat PAI membrane and pure XDA-β-CD. Using Equation (4), estimated amount of cyclodextrin per unit membrane area was calculated, given that all the TGA samples of the cross-linked membranes were prepared with the same membrane area.

[0069] Figure 3 is a graph showing estimated amount of cyclodextrin per unit surface area of cross-linked PAI-CD membrane under various modification time. The estimated amounts of cyclodextrin per unit surface area were calculated using TGA. From the figure, it can be seen that amount of cyclodextrin per unit surface area increases with modification time until about 1 hour. Subsequently, a decrease in amount of cyclodextrin was observed with further modification time. Therefore, according to one embodiment of the present invention, reaction equilibrium exists in the cross-linking reaction, wherein a maximum degree of reaction is achieved at about 1 hour.

[0070] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising”, “including,” “containing”, etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by exemplary embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0071] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative

limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0072] Other embodiments are within the following claims. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will
5 recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

What is claimed is:

1. A process for making a cross-linked polymer, the process comprising
 - 5 a. exposing the polymer to a cross-linking agent, the cross-linking agent comprising at least one cyclodextrin moiety, the cyclodextrin moiety containing at least one reactive group, and
 - b. allowing the polymer and the cross-linking agent to react via the reactive group so as to form the cross-linked polymer.
- 10 2. The process of claim 1, wherein the reactive group is selected from the group consisting of an amino group, a hydroxyl group, an allyl glycidyl group, an epoxide group, a thiol group, an oxetane group, an internal C=C group, a terminal C=C group, an allyl group, an allyl glycidyl ether group, an internal C≡C group, a terminal C≡C group, an internal coupled -C=C-C=C- group, a terminal coupled -C=C-C=C- group or

15 substituted derivatives thereof.
3. The process of claim 1, wherein the cross-linking agent has the general Formula 1:

$$\text{X-NH-R-NH}_2$$

 wherein X is a cyclodextrin moiety, R is one of an aliphatic, an alicyclic, an aromatic, an arylaliphatic group and a silyl group, having a main chain of about 1 to about 30

20 carbon atoms and 0 to about 10 heteroatoms selected from the group consisting of N, O, S, Se and Si.
4. The process of claim 3, wherein the moiety X of the cross-linking agent is β -cyclodextrin.
5. The process of claim 1, wherein the polymer is selected from the group consisting of

25 optionally substituted polyamide, optionally substituted polyimide, polyamide-imide, polyetherimide, polycarbonate, polysulfone, polyethersulfone, polyester, polyurethane, polyetherketone, poly(phenylene oxide), cellulose acetate, cellulose triacetate, rubbery

polymer, vinyl polymer, polymer/inorganic filler mixed matrix material, copolymer and mixtures thereof.

6. The process of claim 5, wherein the polymer is a poly(imide) or a poly(amide imide).
- 5 7. The process of any one of claims 1 to 6, wherein the cross-linking agent and/or the polymer is provided in a suitable solvent.
8. The process of claim 7, wherein the solvent is one of a ketone, alcohol, acetic acid, formamide, tetrahydrofuran, ethyl acetate, acetonitrile, dimethyl sulfoxide, hexane, benzene, diethyl ether, diethylene glycol dimethyl ether, methylene chloride, carbon tetrachloride, trichloroethylene, N-methyl pyrrolidinone, and water.
- 10 9. The process of claim 7, wherein the combined amount of cross-linking agent and polymer in the solvent is in the range of about 1 wt% to about 20 wt% of the combined amount of cross-linking agent, polymer and solvent.
- 15 10. The process according to any one of claims 1 to 9, wherein the process comprises providing a membrane in solid form to which a solution comprising a cross-linking agent is added.
11. A polymer obtainable by a process according to any one of claims 1 - 9.
12. The polymer of claim 11, wherein the amount of cyclodextrin in the polymer is in the range of about 0.01 wt% to about 50 wt% of the combined amount of cyclodextrin and polymer.
- 20 13. The polymer of claim 11, wherein the amount of cyclodextrin in the polymer is in the range of about 0.01 wt% to about 15 wt% of the combined amount of cyclodextrin and polymer.
- 25 14. The polymer of claim 11, wherein the amount of cyclodextrin in the polymer is in the range of about 0.01 wt% to about 5 wt% of the combined amount of cyclodextrin and polymer.
15. The use of a polymer according to any one of claims 11 - 14 in formation of a membrane.

16. A membrane obtainable by the process according to claim 10.

17. The use of a membrane as recited in claim 15 or 16 in the separation of isomers.

18. The use of a membrane as recited in claim 15 or 16 in the separation of structural isomers.

5 19. The use of a membrane as recited in claim 15 or 16 in the separation of stereoisomers.

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