CLAIMS

1. An interfacial polymerisation process for forming a thin film composite membrane for gas separation or liquid filtration, the process comprising the steps of:

(a) impregnating a porous support membrane with a first reactive monomer solution comprising :

(i) a first solvent for the said first reactive monomer;

(ii) a first reactive monomer;

(iii) optionally, an activating solvent being a polar aprotic solvent,

(iv) optionally, additives including alcohols, ketones, ethers, esters, halogenated hydrocarbons, nitrogen-containing compounds and sulphur-containing compounds, monohydric aromatic compounds;

(b) contacting the impregnated support membrane with a second reactive monomer solution comprising:

(i) a second solvent for the second reactive monomer;

(ii) a second reactive monomer;

(iii) optionally, additives including alcohols, ketones, ethers, esters, halogenated hydrocarbons, nitrogen-containing compounds and sulphur-containing compounds, monohydric aromatic compounds;

wherein:

the first solvent and the second solvent form a two phase system;

at least one of the first and second reactive monomers possesses concavity; and

the reaction of the first and second reactive monomers results in the in-situ formation of a covalently cross-linked 3-dimensional polymeric network possessing a continuous network of interconnected intermolecular voids, said voids arising from the structure of the first and second monomers;

(c) optionally, after a reaction period, capping the unreacted groups of the separating layer with functional groups to modify the surface chemistry;

(d) after a reaction period, immersing the resulting composite membrane into a quench medium; and

(e) optionally, curing the membrane with temperature or microwaves for a given time.

2. A process according to claim 1, wherein the support membrane is formed from:
i) an inorganic material including silicon carbide, silicon oxide, zirconium oxide, titanium oxide, aluminium oxides or zeolites, or
ii) one of the following polymers or a mixture thereof, some of which may be optionally crosslinked: polysulfone, polyethersulfone, poly(ether sulfone ketone), polyacrylonitrile, polypropylene, polyamide, cellulose acetate, cellulose diacetate, cellulose triacetate, poly(ether ethyl ketone), poly (pthalazinone ether sulfone ketone), a perfluoropolymer, polyimide, polybenzimidazole, perfluropolymers, polyether ether ketone (PEEK), sulfonated polyether ether ketone (S-PEEK), or other porous polymeric support membrane.

3. A process according to claim 1 or claim 2, wherein either or both of the support membrane and the resulting thin film composite membrane is treated with a conditioning agent selected from one or more of synthetic oils (including polyolefinic oils, silicone oils, polyalphaolefinic oils, polyisobutylene oils, synthetic wax isomerate oils, ester oils and alkyl aromatic oils), mineral oils (including solvent refined oils and hydroprocessed mineral oils and petroleum wax isomerate oils), vegetable fats and oils, higher alcohols (such as decanol, dodecanol, heptadecanol), glycerols, and glycols (such as polypropylene glycols, polyethylene glycols, polyalkylene glycols).

4. A process according to any one of claims 1, 2 or 3, wherein the first reactive monomer solution comprises an aqueous solution of a salt of a polyphenol or polyamine which possesses concavity.

5. A process according to any preceding claim, wherein the first reactive monomer comprises at least one spiro-contorted centre, at least one bridged ring moiety and/or sterically congested single covalent bonds around which there is restricted rotation

6. A process according to any preceding claim, wherein the first reactive monomer is selected from one or more of the group consisting of 1,1-spirobisindanes, 9,9-spirobisfluorenes, bisnaphthalenes, 1,1-spirobis,2,3,4-tetrahydro-naphthalenes, and 9,10-ethanoanthracene.

7. A process according to any preceding claim, wherein the first reactive monomer solution comprises an aqueous solution of a salt of 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-

spirobisindane.

8. A process according to any preceding claim, wherein the second reactive monomer solution contains mono-acyl chlorides, polyacyl chlorides or a mixture thereof, or other monomers.

9. A process according to any preceding claim, wherein the second reactive monomer solution contains trimesoyl chloride, iso-phthaloyl dichloride, or sebacoyl chloride or a mixture thereof.

10. A process according to any preceding claim, wherein the composite membrane is treated with an activating solvent being a polar aprotic solvent.

11. A process according to claim 10, wherein composite membrane is treated with an activating solvent by filtration through the membrane using the activating solvent.

12. A process according to any preceding claim, wherein the composite membrane is treated with an activating solvent comprising DMF, NMP, DMSO, DMAc or a mixture thereof.

13. A process according to any preceding claim in which the contacting time in step (b) is chosen from between 1 second and 5 hours.

14. A process according to any preceding claim in which the temperature of the contacting step (b) solution is held between 10 and 100°C.

15. A thin film composite membrane for gas separation or liquid filtration, comprising a support membrane coated with a separating layer having intrinsic microporosity, wherein the separating layer comprises first and second monomers, at least one of the first and second monomers having concavity, the first and second monomers being polymerised to form a covalently cross-linked 3-dimensional polymeric network possessing a continuous network of interconnected intermolecular voids, said voids arising from the structure of the first and second monomers.

CLAIMS

1. A thin film composite membrane for gas separation or liquid filtration, comprising a support membrane coated with a separating layer, wherein the separating layer comprises a network polymer possessing intrinsic microporosity.

2. A membrane according to claim 1, wherein the support membrane is impregnated with a conditioning agent.

3. A membrane according to claim 1 or claim 2, wherein the support membrane is stable in polar aprotic solvents.

4. A membrane according to any one of the preceding claims, wherein unreacted functional groups in the separating layer are capped to change the surface chemistry.

5. A membrane according to any one of the preceding claims, wherein the membrane is a temperature or microwave cured membrane.

6. A membrane according to any one of the preceding claims, wherein the composite membrane is optionally treated with an activating solvent prior to use in nanofiltration.

7. A membrane according to any one of the preceding claims, wherein at least one monomeric component of the network polymer possesses concavity.

8. A membrane according to claim 7, wherein the monomeric component possessing concavity is selected from a di- or poly- nucleophile, or a di- or poly- electrophile having two or more functional groups.

9. A membrane according to claim 7 or claim 8, wherein the monomeric component possessing concavity comprises at least one spiro-contorted centre, at least one bridged ring moiety and/or sterically congested single covalent bonds around which there is restricted rotation.

10. A membrane according to any one of claims 7 to 9, wherein the monomers possessing concavity are selected from one or more of the group consisting of 1,1-spirobisindanes, 9,9-spirobisfluorenes, bisnaphthalenes, 1,1-spirobis,2,3,4-tetrahydro-naphthalenes, and 9,10-ethanoanthracene.

11. A membrane according to any one of claims 7 to 9, wherein the monomers possessing concavity are selected from oligomers comprising a first generally planar species connected by rigid linkers having a point of contortion such that two adjacent first planar species connected by the linker are held in non-coplanar orientation.

12. A membrane according to any one of the preceding claims, wherein the separating layer comprises at least one of aliphatic or aromatic polyamide, aromatic polyhydrazide, poly-benzimidazolone, polyepiamine/amide, polyepiamine/urea, poly-ethyleneimine/urea, sulfonated polyfurane, polybenzimidazole, polypiperazine isophtalamide, a polyether, a polyether-amide, a polyether-urea, a

polyester, polyester-amide or a polyimide or a copolymer thereof or a mixture thereof.

13. A membrane according to any one of the preceding claims in which the separating layer comprises of diphenol, triphenol, polyphenol, trimesoyl halide and tetraphenolspirobisindane, trimesoyl chloride and 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane.

14. A membrane according to any one of the preceding claims in which the support membrane is formed from one of the following polymers or a mixture thereof, some of which may be optionally crosslinked: polysulfone, polyethersulfone, poly(ether sulfone ketone), polyacrylonitrile, polypropylene, polyamide, cellulose acetate, cellulose diacetate, cellulose triacetate, poly(ether ethyl ketone), poly (pthalazinone ether sulfone ketone), a perfluoropolymer, polyimide, polybenzimidazole, perfluropolymers, polyether ether ketone (PEEK), sulfonated polyether ether ketone (S-PEEK), or other porous polymeric support membrane.

15. A membrane according to claim 14, wherein the support membrane is a crosslinked polyimide support membrane and the polyimide used to form the support membrane is at least one copolymer derived from (a) the co-condensation of benzophenone 3,3',4,4'-tetracarboxylic acid dianhydride and a mixture of (i) di(4-aminophenyl) methane and toluene diamine, or (ii) a mixture of 4,4'-methylenebis (phenyl isocyanate) and toluene diisocyanate; or (b) the condensation of 1H,3H-Benzo[1,2-c:4,5-c']difuran-1,3,5,7-tetrone with 5,5'-carbonylbis[1,3-isobenzofurandione], 1,3-diisocyanato-2-methylbenzene and 2,4-diisocyanato-1-methylbenzene.

16. A membrane according to any one of claims 1 to 13 in which the support membrane is formed from an inorganic material including silicon carbide, silicon oxide, zirconium oxide, titanium oxide, aluminium oxides or zeolites.

17. A membrane according to any one of the preceding claims, in which the support membrane comprises crosslinks formed from the reaction of aliphatic amines, aliphatic-aromatic amines and aromatic amines with a polyimide polymer.

18. A membrane according to any one of the preceding claims in which the support membrane is impregnated with a non-volatile liquid conditioning agent.

19. A membrane according to claim 18, wherein the conditioning agent is selected from one or more of synthetic oils (including polyolefinic oils, silicone oils, polyalphaolefinic oils, polyisobutylene oils, synthetic wax isomerate oils, ester oils and alkyl aromatic oils), mineral oils (including solvent refined oils and hydroprocessed mineral oils and petroleum wax isomerate oils), vegetable fats and oils, higher alcohols (such as decanol, dodecanol, heptadecanol), glycerols, and glycols (such as polypropylene glycols, polyethylene glycols, polyalkylene glycols).

20. A composite membrane according to claim 6, wherein the activating solvent is a polar aprotic

solvent.

21. Use of a membrane of any one of claims 1-20 for nanofiltration of a feed stream solution comprising a solvent and dissolved solutes.

22. Use of a membrane as in any of claims 1-20 for separation of a gas stream into component mixtures.

23. An interfacial polymerisation process for forming a thin film composite membrane according to claim 1, comprising the steps of:

(a) impregnating a porous support membrane which may comprise a first conditioning agent, with a first reactive monomer solution comprising :

(i) a first solvent for the said first reactive monomer;

(ii) a first reactive monomer or/and a reactive monomer possessing concavity;

(iii) optionally, an activating solvent,

(iv) optionally, additives including alcohols, ketones, ethers, esters, halogenated hydrocarbons, nitrogen-containing compounds and sulphur-containing compounds, monohydric aromatic compounds;

(b) contacting the impregnated support membrane with a second reactive monomer solution comprising:

(i) a second solvent for the second reactive monomer;

(ii) a second reactive monomer or/and a reactive monomer possessing concavity;

(iii) optionally, additives including alcohols, ketones, ethers, esters, halogenated hydrocarbons, nitrogen-containing compounds and sulphur-containing compounds, monohydric aromatic compounds;

wherein:

the first solvent and the second solvent form a two phase system;

at least one of the reactive monomers possesses concavity; and

the reaction of the monomers results in a separating layer forming on the support membrane to give a composite membrane;

(c) optionally, after a reaction period, capping the unreacted groups of the separating layer with functional groups to modify the surface chemistry;

(d) after a reaction period, immersing the resulting composite membrane into a quench medium;

(e) optionally, curing the membrane with temperature or microwaves for a given time;

(f) optionally, treating the resulting composite membrane with an activating solvent; and

(g) optionally, impregnating the resulting composite membrane with a second conditioning agent.

24. A process according to claim 23, wherein the support membrane is formed from one of the following polymers or a mixture thereof, some of which may be optionally crosslinked: polysulfone, polyethersulfone,

poly(ether sulfone ketone), polyacrylonitrile, polypropylene, polyamide, cellulose acetate, cellulose diacetate, cellulose triacetate, poly(ether ethyl ketone), poly (pthalazinone ether sulfone ketone), a perfluoropolymer, polyimide, polybenzimidazole, perfluropolymers, polyether ether ketone (PEEK), sulfonated polyether ether ketone (S-PEEK), or other porous polymeric support membrane.

25. A process according to claim 23 or claim 24, wherein the first and/or second conditioning agent is selected from one or more of synthetic oils (including polyolefinic oils, silicone oils, polyalphaolefinic oils, polyisobutylene oils, synthetic wax isomerate oils, ester oils and alkyl aromatic oils), mineral oils (including solvent refined oils and hydroprocessed mineral oils and petroleum wax isomerate oils), vegetable fats and oils, higher alcohols (such as decanol, dodecanol, heptadecanol), glycerols, and glycols (such as polypropylene glycols, polyethylene glycols, polyalkylene glycols).

26. A process according to any one of claims 23 to 25, wherein the first reactive monomer solution comprises an aqueous solution of a salt of a polyphenol or polyamine which possesses concavity.

27. A process according to any of claims 23 to 25, wherein the first reactive monomer solution comprises an aqueous solution of a salt of 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane.

28. A process according to any one of claims 23 to 27, wherein the first reactive monomer solution contains ethylene glycol, propylene glycol, glycerine, polyethylene glycol, polypropylene glycol, and copolymers of ethylene glycol and propylene glycol, or polar aprotic solvents.

29. A process according to any one of claims 23 to 28, wherein the second reactive monomer solution may contain mono-acyl chlorides, polyacyl chlorides or a mixture thereof, or other monomers.

30. A process according to any one of claims 23 to 29, wherein the second reactive monomer solution contains trimesoyl chloride, iso-phthaloyl dichloride, or sebacoyl chloride or a mixture thereof.

31. A process according to any one of claims 23 to 30, wherein the unreacted groups in the thin film polymer network are optionally capped in step (c) with reactive groups.

32. A process according to any one of claims 23 to 31, wherein composite membrane is optionally cured in step (e) with temperature or with microwaves.

33. A process according to any one of claims 23 to 32, wherein composite membrane is treated in step (f) with an activating solvent by immersion or washing in the activating solvent.

34. A process according to any one of claims 23 to 32, wherein composite membrane is treated in step (f) with an activating solvent by filtration through the membrane using the activating solvent.

35. A process according to any one of claims 23 to 34, wherein composite membrane is treated in step (f) with an activating solvent comprising DMF, NMP, DMSO, DMAc or a mixture thereof.

36. A process according to any of claims 23 to 35 in which the contacting time in step (b) is chosen from between 1 second and 5 hours.

37. A process according to any of claims 23 to 36 in which the temperature of the contacting step (b) solution is held between 10 and 100°C.

38. A process according to any of claims 23 to 37 in which the second conditioning agent in step (b) is a non-volatile liquid.

39. A process according to any of claims 23 to 38 in which the second conditioning agent in step (b) is selected from one or more of synthetic oils (including polyolefinic oils, silicone oils, polyalphaolefinic oils, polyisobutylene oils, synthetic wax isomerate oils, ester oils and alkyl aromatic oils), mineral oils (including solvent refined oils and hydroprocessed mineral oils and petroleum wax isomerate oils), vegetable fats and oils, higher alcohols (such as decanol, dodecanol, heptadecanol), glycerols, and glycols (such as polypropylene glycols, polyethylene glycols, polyalkylene glycols).

40. A process according to any of claims 23 to 39 in which the resulting membrane is configured as flat sheets, hollow fibres, spiral wound, plate and frame, shell and tube, or derivative designs thereof.