CLAIMS

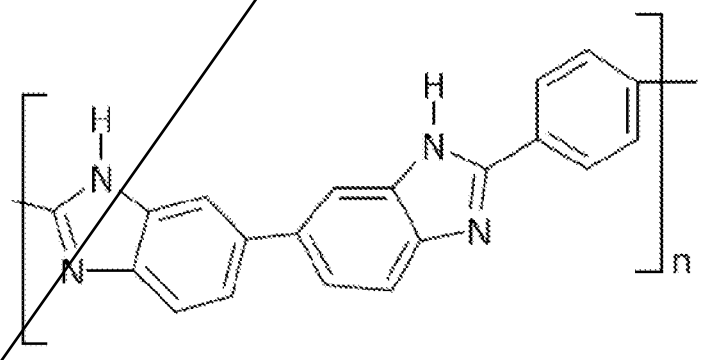
1. A membrane for nanofiltration of a feed stream solution comprising a solvent and dissolved solutes and showing preferential rejection of the solutes at ambient temperature, comprising an integrally skinned asymmetric polybenzimidazole membrane, wherein the membrane is impregnated with a conditioning agent that maintains the pore structure of the membrane prior to its use for nanofiltration.

2. A membrane according to claim 1 in which the polybenzimidazole membrane is crosslinked.

3. A membrane according to claim 1 or claim 2, wherein the dissolved solutes have molecular weights in the range 200-2000 g mol^{-1}.

4. A membrane according to any one of claims 1 to 3, wherein the solvent is an organic solvent and the membrane is stable thereto.

5. The membrane according to any one of claims 1 to 4, wherein the polybenzimidazole polymer has the following formula:



6. A membrane according to any one of the preceding claims, wherein a discrete organic matrix is dispersed in the crosslinked polybenzimidazole asymmetric membrane at amounts up to 50 % by weight of said membrane.

7. A membrane according to any one of the preceding claims, wherein a discrete inorganic matrix is dispersed in the crosslinked polybenzimidazole asymmetric membrane at amounts up to 50% by weight of said dope solution.

8. A membrane according to claim 6 or claim 7, wherein the average particle size of the discrete matrix is less than 0.1 micron.

9. A membrane according to any one of the preceding claims, comprising crosslinks formed from the reaction of multifunctional halides, divinyl sulfone, or strong polyfunctional organic acids with the polybenzimidazole polymer;

10. A membrane according to any one of the preceding claims, comprising crosslinks formed from the reaction of polybenzimidazole with dibromobutane, tribromopropane, trichloropropane, pentaerythrityl tetrabromide, pentaerythrityl tetrachloride, divinyl sulfones, perfluoroglutaric acid, benzene hexacarboxylic acid, benzene pentacarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,3,5-benzenetricarboxylic acid, dibromosuccinic acid, polyacrylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 2,6-naphthalenedisulfonic acid, aryl-sulfonic acids, aryl-sulfinic acids, aryl-phosphinic acids, aryl-phosphonic acids.

11. A membrane according to any one of the preceding claims, wherein the conditioning agent is a non-volatile liquid.

12. A membrane according to any one of the preceding claims , 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 or derivatives thereof (such as polypropylene glycols, polyethylene glycols, polyalkylene glycols or derivatives thereof).

13. Use of a membrane according to any of claims 1-12 for nanofiltration of a feed stream solution comprising a solvent and dissolved solutes.

14. Use of a membrane according to claim 13, wherein the feed stream comprises at least one strongly basic solvent.

15. Use of a membrane according to claim 13, wherein the feed stream comprises at least one strongly acidic solvent.

16. A process for forming an integrally skinned asymmetric crosslinked polybenzimidazole membrane for solvent nanofiltration, comprising the steps of:
(a) preparing a polybenzimidazole dope solution comprising:
(i) a polybenzimidazole polymer, and (ii) a solvent system for said polybenzimidazole which is water miscible;
(b) casting a film of said dope solution onto a supporting substrate;
(c) allowing the dope solution to evaporate for an evaporation period, and then immersing the film cast on the substrate into a coagulating medium;
(d) treating the resulting asymmetric membrane with a solvent comprising one or more of a multifunctional alkyl halide, a divinyl sulfone, a strong polyfunctional organic acid;
(e) treating the asymmetric membrane with a conditioning agent.

17. A process according to claim 16, wherein the polybenzimidazole polymer is present in amounts of 5 to 30% by weight of said dope solution.

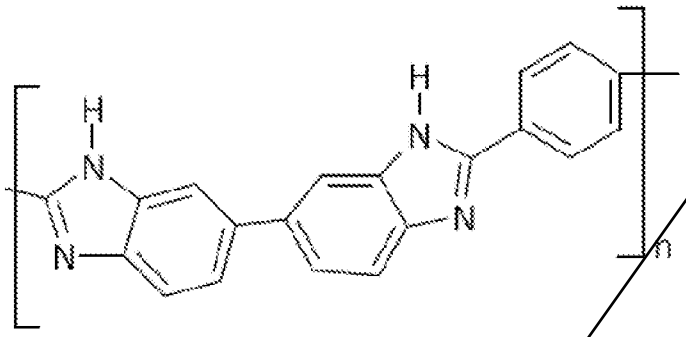
18. A process according to claim 16 or claim 17, wherein the multifunctional alkyl halide is a mono-,di-,tri- functional alkyl halide.

19. A process according to any one of claims 16 to 18, further comprising (f) drying the membrane.

20. A process according to claim any one of claims 16 to 19, wherein the process further comprises a step of heating the membrane to about 150°C or higher, preferably

for up to 3 hours.

21. A process according to any one of claims 16 to 20, wherein the polybenzimidazole has the following formula:



22. A process according to any one of claims 16 to 21 wherein the polybenzimidazole dope solution comprises solvents chosen from N-methyl-2-pyrrolidone, tetrahydrofuran, N,N-dimethylformamide, dimethylsulfoxide, N,N-dimethylacetamide, 1,4 dioxane, gamma.-butyrolactone, water, alcohols, ketones, and formamide.

23. A process according to any one of claims 16 to 22, wherein the polybenzimidazole dope solution further comprises a viscosity enhancer in amounts of up to 10% by weight of said dope solution.

24. A process according to any one of claims 16 to 23, wherein the polybenzimidazole dope solution further comprises a viscosity enhancer chosen from polyvinyl pyrrolidones, polyethylene glycols and urethanes added to the polybenzimidazole dope solution at amounts up to 10% by weight of said dope solution.

25. A process according to any one of claims 16 to 24, wherein the polybenzimidazole dope solution further comprises a void suppressor used in amounts up to 5% of the weight of said polybenzimidazole dope solution.

26. A process according to any one of the preceding claims 16 to 25, wherein the polybenzimidazole dope solution further comprises a discrete organic matrix dispersed in the polybenzimidazole dope solution at amounts up to 20 % by weight of said dope solution.

27. A process according to any one of the preceding claims 16 to 25, wherein the polybenzimidazole dope solution further comprises a discrete inorganic matrix dispersed in the polybenzimidazole dope solution at amounts up to 20% by weight of said dope solution.

28. A process according to claim 26 or claim 27, wherein the average particle size of the discrete matrix is less than 0.1 micron.

29. A process according to any one of claims 26 to 27 in which the discrete matrix is first dispersed in a solvent and subsequently added to the dope solution.

30. A process according to claim 29 in which the solvent used to disperse the discrete matrix is removed from the polybenzimidazole dope solution by evaporation.

31. A process according to any one of claims 16 to 30 in which the crosslinking agent is chosen from multifunctional alkyl halides, divinyl sulfones, strong polyfunctional organic acids.

32. A process according to any one of claims 16 to 31 in which the crosslinking agent is chosen from alkyl halides (including dibromobutane, tribromopropane, trichloropropane, pentaerythrityl tetrabromide, and pentaerythrityl tetrachloride), divinyl sulfones, perfluoroglutaric acid, benzene hexacarboxylic acid, benzene pentacarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,3,5-benzenetricarboxylic acid, dibromosuccinic acid, polyacrylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 2,6-naphthalenedisulfonic acid, aryl-sulfonic acids, aryl-sulfinic acids, aryl-phosphinic acids, aryl-phosphonic acids.

33. A process according to any one of claims 16 to 34 in which the crosslinking agent is dissolved in a solvent.

34. A process according to any one of claims 16 to 33, wherein the crosslinking agent is dissolved in a solvent chosen from ketones, ethers, carboxylic acids and alcohols

35. A process according to any one of claims 16 to 34 in which the quantity of crosslinking agent used to treat the polybenzimidazole membrane is adjusted so that the reactive groups in the crosslinking agent and polybenzimidazole amine hydrogen groups in the membrane treated is in the range 0.01 to 100.

36. A process according to any one of claims 16 to 34 in which the quantity of crosslinking agent used to treat the polybenzimidazole membrane is adjusted so that the reactive groups in the crosslinking agent and polybenzimidazole amine hydrogen groups in the membrane treated is in the range 0. 1 to 10.

37. A process according to any one of claims 16 to 36 in which the time for crosslinking is chosen from between 0.1 and 120 hours.

38. A process according to any one of claims 16 to 37 in which the temperature of crosslinking solution is held between 20 and 150°C.

39. A process according to any one of claims 16 to 38 in which the conditioning agent is a non-volatile liquid.

40. A process according to any one of claims 16 to 39 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).

41. A process according to any one of claims 16 to 43 in which the resulting membrane is configured as spiral wound, plate and frame, shell and tube, or derivative designs thereof.

CLAIMS

1. A process for forming an integrally skinned asymmetric crosslinked polybenzimidazole membrane for solvent nanofiltration, comprising the steps of:

(a) preparing a polybenzimidazole dope solution comprising:

(i) a polybenzimidazole polymer, and (ii) a solvent system for said polybenzimidazole which is water miscible;

(b) casting a film of said dope solution onto a supporting substrate;

(c) allowing the dope solution to evaporate for an evaporation period, and then immersing the film cast on the substrate into a coagulating medium;

(d) treating the resulting asymmetric membrane with a solvent comprising one or more of a multifunctional alkyl halide, a divinyl sulfone, a strong polyfunctional organic acid;

(e) treating the asymmetric membrane with a conditioning agent.

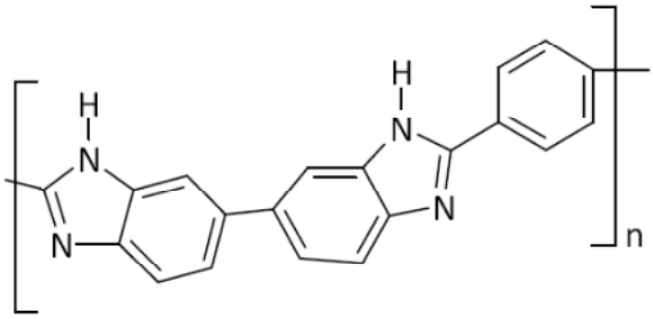
2. A process according to claim 1, wherein the polybenzimidazole polymer is present in amounts of 5 to 30% by weight of said dope solution.

3. A process according to claim 1 or claim 2 wherein the multifunctional alkyl halide is a mono-,di-,tri- functional alkyl halide.

4. A process according to any one of claims 1, 2, or 3, further comprising (f) drying the membrane;

and/or optionally wherein the process further comprises a step of heating the membrane to about 150°C or higher, preferably for up to 3 hours.

5. A process according to any preceding claim, wherein the polybenzimidazole has the following formula:



optionally wherein the polybenzimidazole dope solution comprises solvents chosen from N-methyl-2-pyrrolidone, tetrahydrofuran, N,N-dimethylformamide, dimethylsulfoxide, N,N-dimethylacetamide, 1,4 dioxane, gamma.-butyrolactone, water, alcohols, ketones, and formamide.

6. A process according to any preceding claim, wherein the polybenzimidazole dope solution further comprises a viscosity enhancer in amounts of up to 10% by weight of said dope solution;
optionally wherein the polybenzimidazole dope solution further comprises a viscosity enhancer chosen from polyvinyl pyrrolidones, polyethylene glycols and urethanes added to the polybenzimidazole dope solution at amounts up to 10% by weight of said dope solution.
and/or optionally wherein the polybenzimidazole dope solution further comprises a void suppressor used in amounts up to 5% of the weight of said polybenzimidazole dope solution.

7. A process according to any preceding claim, wherein the polybenzimidazole dope solution further comprises a discrete organic or inorganic matrix dispersed in the polybenzimidazole dope solution at amounts up to 20 % by weight of said dope solution;
optionally wherein the average particle size of the discrete matrix is less than 0.1 micron;
and/or optionally wherein the discrete matrix is first dispersed in a solvent and subsequently added to the dope solution;
optionally wherein the solvent used to disperse the discrete matrix is removed from the polybenzimidazole dope solution by evaporation.

8. A process according to any preceding claim, wherein the crosslinking agent is chosen from multifunctional alkyl halides, divinyl sulfones, strong polyfunctional organic acids;
optionally wherein the crosslinking agent is chosen from alkyl halides (including dibromobutane, tribromopropane, trichloropropane, pentaerythrityl tetrabromide, and pentaerythrityl tetrachloride), divinyl sulfones, perfluoroglutaric acid, benzene hexacarboxylic acid, benzene pentacarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,3,5-benzenetricarboxylic acid, dibromosuccinic acid, polyacrylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 2,6-naphthalenedisulfonic acid, aryl-sulfonic acids, aryl-sulfinic acids, aryl-phosphinic acids, aryl-phosphonic acids;
and/or optionally wherein the crosslinking agent is dissolved in a solvent;

optionally wherein the crosslinking agent is dissolved in a solvent chosen from ketones, ethers, carboxylic acids and alcohols

9. A process according to any preceding claim, wherein the quantity of crosslinking agent used to treat the polybenzimidazole membrane is adjusted so that the reactive groups in the crosslinking agent and polybenzimidazole amine hydrogen groups in the membrane treated is in the range 0.01 to 100;
optionally wherein the quantity of crosslinking agent used to treat the polybenzimidazole membrane is adjusted so that the reactive groups in the crosslinking agent and polybenzimidazole amine hydrogen groups in the membrane treated is in the range 0. 1 to 10.

10. A process according to any preceding claim, wherein the time for crosslinking is chosen from between 0.1 and 120 hours;
and/or optionally wherein the temperature of crosslinking solution is held between 20 and 150°C.

11. A process according to any preceding claim, wherein the conditioning agent is a non-volatile liquid;
optionally 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).

12. A process according to any preceding claim, wherein the resulting membrane is configured as spiral wound, plate and frame, shell and tube, or derivative designs thereof.

13. A membrane obtainable by the method of any preceding claim.

14. Use of a membrane according to claim 13 for nanofiltration of a feed stream solution comprising an organic solvent and dissolved solutes, wherein the feed stream comprises at least one strongly basic or strongly acidic solvent.

15. A membrane for nanofiltration of a feed stream solution comprising an organic solvent and dissolved solutes and showing preferential rejection of the solutes at ambient temperature, comprising an integrally skinned asymmetric polybenzimidazole cast film membrane, wherein the membrane is impregnated with a conditioning agent that maintains the pore structure of the membrane prior to its use for nanofiltration.