

CLAIMS

1. A process for preparing a hollow fiber comprising the steps of:

a) providing a dope solution comprising polyamide imide (PAI),

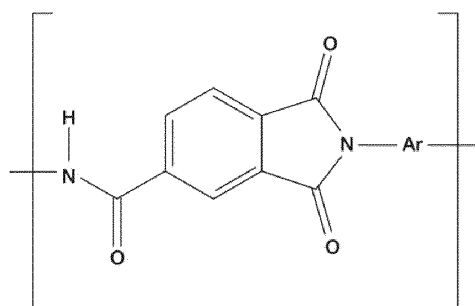
b) providing an aqueous bore solution comprising polyethylene imine (PEI),

5 c) extruding the dope solution in a cross-sectional annular shape and ejecting the bore solution in the center of the annular shape,

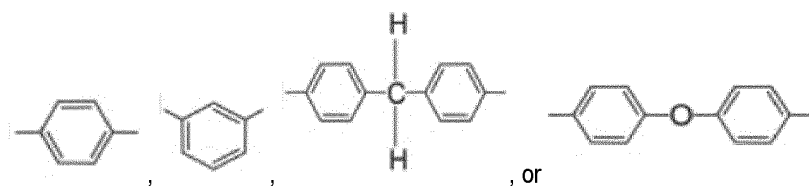
d) allowing the PAI and the PEI to react, thereby forming an internal surface layer comprising the cross-linked reaction product, and

10 e) forming a polyamide Thin Film Composite (TFC) layer by interfacial reaction of aqueous di- or triamine compound and organic di- or triacylhalide compound on the internal surface layer comprising the cross-linked reaction product.

2. The process according to claim 1, wherein the monomer of the PAI has the following chemical structure:



in which Ar is an aromatic group selected from



3. The process according to claim 1 or 2, wherein the dope solution further comprises an aprotic solvent.

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4. The process according to claim 3, wherein the aprotic solvent is selected from the group consisting of N-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and dimethylformamide (DMF), or mixtures thereof.

5 5. The process according to any one of claims 1 to 4, wherein dope solution further comprises a polymer selected from the group consisting of polyphenylsulfone (PPSU), polyethersulfone (PES), Sulfonated polyethersulfone (SPES), polysulfone (PSU), polyetheretherketone (PEEK), high-temperature sulfone resins, self-reinforced polyphenylene, polybenzimidazole (PBI), polyimide (PI), polyetherimide (PEI), polyphenylene sulfide (PPS), and mixtures thereof.

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6. The process according to any one of claims 1 to 5, wherein the solution viscosity of the PAI in 25% NMP and measured at 40°C is 30,000 cP or less.

15 7. The process according to any one of claims 1 to 6, wherein the dope solution further comprises a glycol.

8. The process according to claim 7, wherein the glycol is selected among ethylene glycol, 1,2-propylene glycol, 1,3-propylenen glycol, glycerol or polyethylene glycol(PEG).

20 9. The process according to any one of claims 1 to 8, wherein the PEI of the aqueous bore solution has an average molecular weight (M_w) of 100,000 g/mol or above.

10. The process according to claim 9, wherein the PEI is branched.

25 11. The process according to any one of claims 1 to 10, wherein the aqueous bore solution further comprises an aprotic solvent.

30 12. The process according to claim 11, wherein the aprotic solvent is selected from the group consisting of N-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and dimethylformamide (DMF), or mixtures thereof.

13. The process according to any one of claims 1 to 12, wherein step c) is performed by dry-jet wet spinning.

14. The process according to any one of claims 1 to 13, wherein the nascent hollow fiber after
5 extrusion is moved through an air gap before being coagulated in a non-solvent.

15. The process according to any one of claims 1 to 14, wherein the air gap is between 5 and 40 cm.

10 16. The process according to any one of claims 1 to 15, wherein a plurality of the hollow fibers is assembled in a module before the polyamide TFC layer is formed.

17. The process according to any one of claims 1 to 16, wherein the di- or triamine compound is selected among *m*-phenylenediamine (MPD), diethylene triamine, dipropylene triamine,
15 phenylenetriamine, bis(hexamethylene)triamine, bis(hexamethylene)triamine, bis(3-aminopropyl)-amine, hexamethylenediamine, N-tallowalkyl dipropylene, 1,3,5-triazine-2,4,6-triamine, and mixtures of these compounds.

18. The process according to any one of claims 1 to 17, wherein the di- or triacyl halide compound
20 is selected among trimesoyl chloride (TMC), trimesoyl bromide, isophthaloyl chloride (IPC), isophthaloyl bromide, terephthaloyl chloride (TPC), terephthaloyl bromide, adipoyl chloride, cyanuric chloride and mixtures of these compounds.

19. The process according to any one of claims 1 to 18, wherein aquaporin water channels are
25 incorporated into the TFC layer.

20. The process according to claim 19, wherein the aquaporin water channels are assembled in a nanostructure comprising polyethylene imine.

21. The process according to claim 20, wherein the polyethyleneimine has an average molecular weight of between about 2,000 Da to about 10,000 Da, such as between about 3,000 Da to about 5,000 Da.

5 22. The process according to any one of claims 19 to 21, wherein the aquaporin water channel is solubilized in a detergent prior to the assembling in a nanostructure comprising polyethyleneimine.

23. The process according to claim 22, wherein the detergent is selected from the group consisting of lauryl dimethylamine N-oxide (LDAO), octyl glucoside (OG), dodecyl maltoside (DDM) or a
10 combination thereof.

24. The process according to claim 19, wherein the aquaporin water channels are provided in a vesicle prior to the incorporation in the TFC layer.

15 25. The process according to claim 24, wherein the vesicle comprises an amphiphilic diblock copolymer of the PMOXA-PDMS type and a reactive end group functionalized PDMS.

26. The method according to claim 24 or 25, wherein said PMOXA-PDMS is selected from the group consisting of PMOXA₁₀₋₄₀-PDMS₂₅₋₇₀ and mixtures thereof.

20 27. The method according to claim 26, wherein the mixture comprises at least a first amphiphilic diblock copolymer of the general formula PMOXA₁₀₋₂₈-PDMS₂₅₋₇₀ and a second amphiphilic diblock copolymer of the general formula PMOXA₂₈₋₄₀-PDMS₂₅₋₇₀.

25 28. The method according to anyone of the claims 24 to 27, wherein said reactive end group functionalised PDMS is functionalized with one or more of amine, carboxylic acid, and/or hydroxy groups.

29. The method according to anyone of the claims 24 to 28, further comprising a triblock copolymer
30 of the PMOXA-PDMS-PMOXA type.

30. The method according to anyone of the preceding claims, wherein the TFC layer is present on the inside of the fibers.

31. A hollow fiber comprising an outer support layer, an internal surface layer, and a polyamide Thin Film Composite (TFC) layer, wherein the outer support layer comprises a polyamide imide (PAI), the internal surface layer comprises the reaction product of PAI and polyethylene imine (PEI), and the TFC layer comprises the reaction product of a di- or triamine compound and a di- or triacylhalide compound.

32. The hollow fiber according to claim 31, wherein the outer support layer further comprises a polymer selected from the group consisting of polyphenylsulfone (PPSU), polyethersulfone (PES), polysulfone (PSU), polyetheretherketone (PEEK), high-temperature sulfone resins, self-reinforced polyphenylene, polybenzimidazole (PBI), polyimide (PI), polyetherimide (PEI), polyphenylene sulfide (PPS), and mixtures thereof.

33. The hollow fiber according to claim 31 or 32, wherein the solution viscosity of the PAI in 25% NMP and measured at 40°C is 30,000 cP or less.

34. The hollow fiber according to any one of claims 31 to 33, wherein the PEI has an average molecular weight (M_w) of 100,000 g/mol or above.

35. The hollow fiber according to any one of claims 31 to 34, wherein the PEI is branched.

36. The hollow fiber according to any one of claims 31 to 35, wherein the di- or triamine compound is selected among *m*-phenylenediamine (MPD), diethylene triamine, dipropylene triamine, phenylenetriamine, bis(hexamethylene)triamine, bis(hexamethylene)triamine, bis(3-aminopropyl)-amine, hexamethylenediamine, N-tallowalkyl dipropylene, 1,3,5-triazine-2,4,6-triamine, and mixtures of these compounds.

37. The hollow fiber according to any one of claims 31 to 36, wherein the di- or triacyl halide compound is selected among trimesoyl chloride (TMC), trimesoyl bromide, isophthaloyl chloride

(IPC), isophthaloyl bromide, terephthaloyl chloride (TPC), terephthaloyl bromide, adipoyl chloride, cyanuric chloride and mixtures of these compounds.

38. The hollow fiber according to any one of claims 31 to 37, wherein aquaporin water channels are
5 incorporated into the TFC layer.

39. The hollow fiber according to any one of claims 31 to 38, wherein the aquaporin water channels are assembled in a nanostructure comprising polyethylene imine.

10 40. The hollow fiber according to any one of claims 31 to 39, wherein the polyethyleneimine has an average molecular weight of between about 2,000 Da to about 10,000 Da, such as between about 3,000 Da to about 5,000 Da.

15 41. The hollow fiber according to any one of claims 31 to 40, wherein the aquaporin water channel is solubilized in a detergent prior to the assembling in a nanostructure comprising polyethyleneimine.

20 42. The hollow fiber according to any one of claims 31 to 41, wherein the detergent is selected from the group consisting of lauryl dimethylamine N-oxide (LDAO), octyl glucoside (OG), dodecyl maltoside (DDM) or a combination thereof.

43. The hollow fiber according to any one of claims 31 to 42, wherein the aquaporin water channels are provided in a vesicle.

25 44. The hollow fiber according to any one of claims 31 to 43, wherein the vesicle comprises an amphiphilic diblock copolymer of the PMOXA-PDMS type and a reactive end group functionalized PDMS.

30 45. The hollow fiber according to any one of claims 31 to 44, wherein said PMOXA-PDMS is selected from the group consisting of PMOXA₁₀₋₄₀-PDMS₂₅₋₇₀ and mixtures thereof.

46. The hollow fiber according to any one of claims 31 to 45, wherein the mixture comprises at least a first amphiphilic diblock copolymer of the general formula $\text{PMOXA}_{10-28}\text{-PDMS}_{25-70}$ and a second amphiphilic diblock copolymer of the general formula $\text{PMOXA}_{28-40}\text{-PDMS}_{25-70}$.

5 47. The hollow fiber according to any one of claims 31 to 46, wherein said reactive end group functionalised PDMS is functionalized with one or more of amine, carboxylic acid, and/or hydroxy groups.

10 48. The hollow fiber according to any one of claims 31 to 47, further comprising a triblock copolymer of the PMOXA-PDMS-PMOXA type.

49. The hollow fiber according to anyone of the claims 31 to 48, wherein the wall thickness of the hollow fiber is 0.10 ± 0.01 mm or more.

15 50. The hollow fiber according to anyone of the claims 31 to 49, wherein the inner diameter of the hollow fiber is 0.80 ± 0.01 mm or more.

51. The hollow fiber according to anyone of the claims 31 to 50, wherein the porosity of the hollow fiber is 75% or above.

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52. A hollow fiber obtainable according to anyone of the claims 1 to 30.

53. A hollow fiber module comprising a bundle of hollow fibers according to anyone of the claims 31 to 52.

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54. The hollow fiber module according to claim 53, comprising a shell around the bundle of hollow fibers, an inlet and an outlet connected to the lumen of the hollow fibers in each end of the bundle for passing a first solution through the lumen side of the module, wherein an inlet and an outlet are provided in the shell for passing a second solution through the shell side of the module.

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55. The hollow fiber module according to any one of claims 52 to 54, wherein the bundle of hollow fibers is potted in each end of the module for the formation of a liquid tight sealing between the outer surface of hollow fibers and the shell.