Claims

1) A method of producing polyimide membranes,

wherein the method comprises the steps of:

a) producing a polyimide membrane from

one or more than one dianhydride selected from the group consisting of 3,4,3',4'-benzophenonetetracarboxylic dianhydride, 1,2,4,5-benzenetetracarboxylic dianhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride, oxydiphthalic dianhydride, sulphonyldiphthalic dianhydride, 1,1,1,3,3,3-hexafluoro-2,2-propylidenediphthalic dianhydride,
and
one or more than one diisocyanate selected from the group consisting of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4,6-trimethyl-1,3-phenylene diisocyanate, 2,3,5,6-tetramethyl-1,4-phenylene diisocyanate,

b) annealing the membrane at a temperature in the range from 280°C to the glass transition temperature of the polymer, preferably 280 to 370°C, more preferably 285 to 360°C, still more preferably 290 to 350°C, yet still more preferably at 300 to 340°C, yet still even more preferably at 305 to 330°C and most preferably at 310 to 320°C for the atmosphere surrounding the membrane at a distance of up to 10 cm, preferably 2 to 10 cm, for 15 to 300 min from the time at which the target temperature for the anneal is attained,

wherein
at a pressure of at least 30 mbar, a gas atmosphere having an oxygen content of not more than 0.5% by volume, preferably an inert gas, more preferably nitrogen, of correspondingly low oxygen content surrounds the membrane during the anneal, and/or a corresponding gas stream sweeps around the membrane during the anneal.

2) A method according to Claim 1,

wherein

the anneal is conducted for 30 to 240 min, preferably for 60 to 120 min and more preferably for 60 to 90 min from the time at which the target temperature for the anneal is attained,

and/or wherein

the membranes are heated to the annealing temperature at a heating rate of 0.1 to 10°C/min, preferably 1 to 5°C/min and more preferably 1 to 2°C/min,

and/or wherein

after the temperature of the atmosphere surrounding the membrane at a distance of up to 10 cm, preferably 2 to 10 cm, has permanently dropped to below the maximum annealing temperature down to a temperature of 200 to 275°C, more preferably 200 to 270°C, still more preferably 200 to 250°C and yet still more preferably 200 to 220°C the atmosphere corresponds to the atmosphere defined in Claim 1 and/or the gas stream defined in Claim 1, or in that after the temperature has permanently dropped to below the maximum annealing temperature a vacuum is applied,

and/or wherein

the oxygen content of the atmosphere surrounding the membrane at a distance of up to 10 cm, preferably 2 to 10 cm, is not more than 0.25% by volume and more preferably not more than 0.1% by volume.

3) A method according to either of Claims 1 or 2,

wherein

step a) comprises the sub-steps of

a1) producing a solution of a polyimide polymer in an aprotic dipolar solvent by polymerizing corresponding monomers, the reaction solution comprises 0.01% by weight to 5% by weight, of a basic catalyst and

a2) producing a casting solution comprising the polyimide polymer, and

a3) producing a polyimide membrane from the casting solution,

wherein the casting solution is produced in step a2) from the polymer solution obtained in step a1) without the polyimide between steps a1) and a2) being isolated

in the form of a solid material, particularly not as a dried solid material, and redissolved,

and

wherein the membrane is produced by a phase inversion method.

4) A method according to Claim 3,
wherein
the aprotic dipolar solvent used for producing the polyimide in stage a1) was selected from the group consisting of dimethylformamide, dimethylacetamide, N-methylpyrrolidinone, N-ethylpyrrolidinone, sulpholane, tetrahydrofuran, dioxane or mixtures thereof,

and/or wherein

water-soluble additives are admixed for producing the casting solution in step a2), wherein

the additives used are preferably

volatile water-miscible solvents such as tetrahydrofuran, dioxane or acetone or mixtures thereof

and/or

nonsolvents such as water, methanol, ethanol, n-propanol, isopropanol, butanol, butanediol, ethylene glycol, glycerol, gamma-butyrolactone or mixtures thereof

and/or

pore-formers, preferably polyvinylpyrrolidinone

and/or

water-miscible solvents such as dimethylformamide, dimethylacetamide, N-methylpyrrolidinone, N-ethylpyrrolidinone, sulpholane, dimethyl sulphoxide or mixtures thereof.

5) A method according to either of Claims 1 or 2,

wherein it comprises the following steps within step a):

aI) providing an optionally annealed polyimide polymer in the form of a preferably dried solid material, preferably in the form of a powder or in the form of a pellet material,

aII) producing a casting solution, wherein this casting solution comprises a solvent and the solid material from step aI); and

aIII) forming a hollow fibre membrane from the casting solution.

6) A method according to Claim 5,

wherein

the powder is annealed and/or dried in step aI) by a process of mechanical annealing, thermal annealing or a combination thereof,

and/or wherein

the polymer powder is dried and/or annealed in step aI) at a temperature of 50-250°C, preferably 100 to 200°C, for a period of 6 to 30 hours, preferably 10 to 16 hours.

7) A method according to any one of Claims 3 to 6,

wherein

an integrally asymmetrical hollow fibre membrane is produced in steps a3) or aIII), wherein the hollow fibre is preferably spun from the polyimide casting solution and a bore solution in a continuous process using a two-material die.

8) A method according to Claim 7,

wherein

the spinning die is at a distance of 5 cm to 1 m, preferably 5 to 60 cm from a precipitation bath,

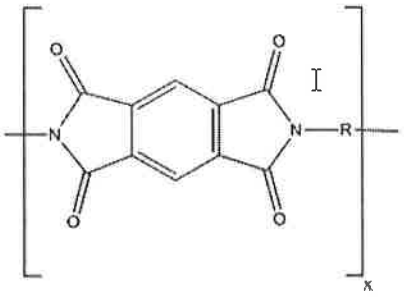
and wherein the hollow fiber before entry into the precipitation bath is, preferably in a shaft, subjected to the flow of a dry gas stream thermostated to 25 to 130°C, more preferably to 30 to 80°C, or is passed through a corresponding gas atmosphere.

9) A method according to Claim 8,

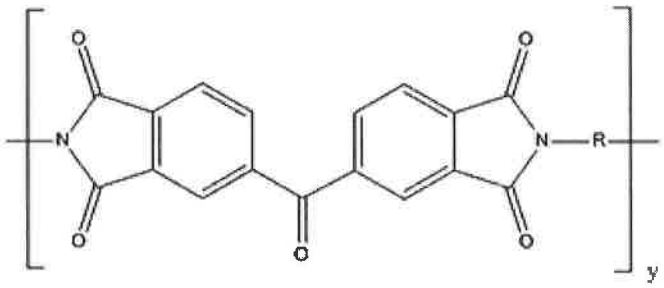
wherein the dry gas stream used is nitrogen, air, argon, helium, carbon dioxide, methane or other industrial inert gases or mixtures thereof,
and/or wherein
the gas velocity in the shaft is between 0.1 and 10 m/min, preferably between 0.5 and 5 m/min and more preferably 1 and 3 m/min.

10) A method according to any preceding claim,
wherein
the membranes were subjected to one or more than one wash with water down to a residual solvent content of not more than 1% by weight, preferably not more than 0.5% by weight, after leaving the precipitation bath and before the anneal,
and/or wherein
the membranes were subjected to a solvent exchange before the anneal, but preferably after the wash,
and/or wherein
the membranes were dried, preferably after the wash, more preferably after the solvent exchange, such that they have a water and/or solvent content of not more than 5% by weight, preferably not more than 3% by weight before the annealing step,
and/or wherein
the membrane haul-off speed is 10 and 80 m/min, preferably between 30 and 70 m/min,
and/or wherein
the membranes before annealing have an oxygen permeance of not less than 25 GPU, preferably not less than 50 GPU, more preferably in the range from 100 to 2000 GPU, still more preferably from 200 to 1500 GPU, yet still more preferably from 300 to 1000 GPU and yet still even more preferably from 400 to 800 GPU.

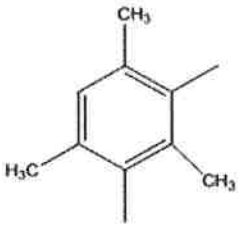
11) A method according to any one of Claims 1 to 10, wherein
the polyimide is a polyimide consisting of monomer units (A) and (B), and wherein:



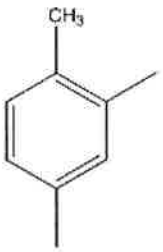
(A)



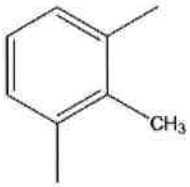
(B)



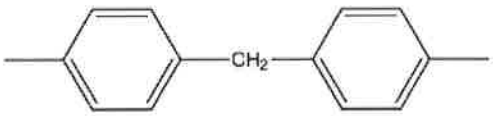
(LI)



(L2)



(L3)



(L4)

where $0 \leq x \leq 0.5$ and $1 \geq y \geq 0.5$ and R represents one or more, identical or different moieties selected from the group consisting of the moieties L1, L2, L3 and L4, preferably in that the polyimide is a polymer where x = 0, y = 1 and R consists of 64 mol% L2, 16 mol% L3 and 20 mol% L4, or is a polymer having the composition x = 0.4, y = 0.6 and R consists of 80 mol% L2 and 20 mol% L3.