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, for the atmosphere surrounding the membrane at a distance of up 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 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 membrane is annealed at a temperature in the range from 280 to 370°C.

3) A method according to Claim 1 or 2,

wherein

the gas atmosphere is nitrogen having an oxygen content of not more than 0.5% by volume.

4) A method according to any one of Claims 1 to 3,

wherein

the anneal is conducted for 30 to 240 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,

and/or wherein

after the temperature of the atmosphere surrounding the membrane at a distance of up to 10 cm has permanently dropped to below the maximum annealing temperature down to a temperature of 200 to 275°C the atmosphere corresponds to the atmosphere defined in Claim 1 and/or the gas stream defined in Claim 1, or wherein 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 is not more than 0.25% by volume.

5) A method according to any one of Claims 1 to 4,

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 and redissolved,

and

wherein the membrane is produced by a phase inversion method.

6) A method according to Claim 5,
wherein
the aprotic dipolar solvent used for producing the polyimide in stage a1) is 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).

7) A method according to Claim 6,

wherein

the water-soluble additives used are

volatile water-miscible solvents selected from tetrahydrofuran, dioxane or acetone and mixtures thereof

and/or

nonsolvents selected from water, methanol, ethanol, n-propanol, isopropanol, butanol, butanediol, ethylene glycol, glycerol, gamma-butyrolactone and mixtures thereof

and/or

polyvinylpyrrolidinone

and/or

water-miscible solvents selected from dimethylformamide, dimethylacetamide, N-methylpyrrolidinone, N-ethylpyrrolidinone, sulpholane, dimethyl sulphoxide and mixtures thereof.

8) A method according to any one of Claims 1 to 4,

wherein

it comprises the following steps within step a):

aI) providing an optionally annealed polyimide polymer in the form of a solid 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.

9) A method according to Claim 8,

wherein

the polyimide polymer is provided in the form of a powder.

10) A method according to Claim 9,

wherein

the powder is annealed 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 for a period of 6 to 30 hours.

11) A method according to any one of Claims 5 to 10,

wherein

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

12) A method according to Claim 11,
wherein
the spinning die is at a distance of 5 cm to 1 m from a precipitation bath,
and wherein the hollow fiber before entry into the precipitation bath is subjected to the flow of a dry gas stream thermostated to 25 to 130°C or is passed through a corresponding gas atmosphere.

13) A method according to Claim 12,
wherein
the dry gas stream used is nitrogen, air, argon, helium, carbon dioxide, methane or other industrial inert gases or mixtures thereof.

14) A method according to Claim 12 or 13,
wherein
the hollow fiber is subjected to the flow of a dry gas stream in a shaft before entry into the precipitation bath.

15) A method according to Claim 14,
wherein
the gas velocity in the shaft is between 0.1 and 10 m/min.

16) A method according to any one of Claims 1 to 15,
wherein
the membranes are subjected to one or more than one wash with water down to a residual solvent content of not more than 1% by weight after leaving the precipitation bath and before the anneal,
and/or wherein
the membranes are subjected to a solvent exchange before the anneal,
and/or wherein
the membranes are dried such that they have a water and/or solvent content of not more than 5% by weight before the annealing step,
and/or wherein

the membrane haul-off speed is between 30 and 70 m/min,

and/or wherein

the membranes before annealing have an oxygen permeance of not less than 25 GPU.

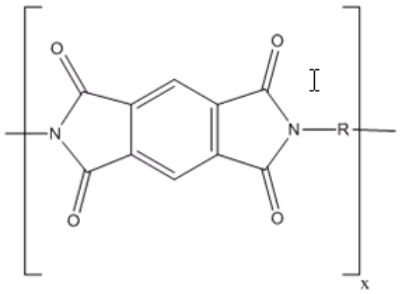
17) A method according to Claim 16,

wherein

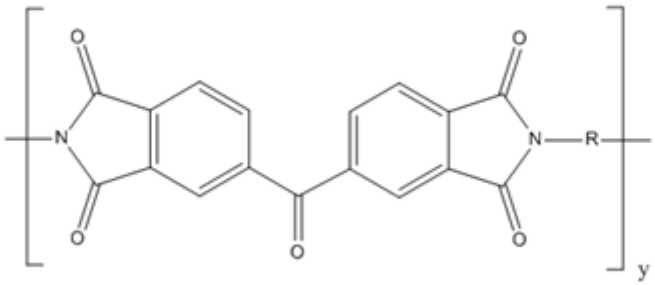
the membranes before annealing have an oxygen permeance in the range from 100 to 2000 GPU.

18) A method according to any one of Claims 1 to 17, wherein

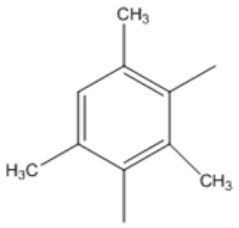
the polyimide is a polyimide consisting of monomer units (A) and (B), wherein:



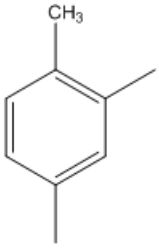
(A)



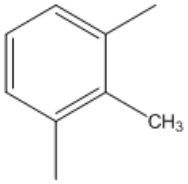
(B)



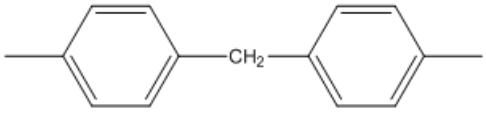
(L1)



(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.

19) A method according to Claim 18,

wherein

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.