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

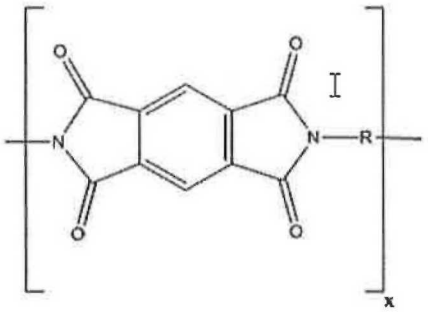
one or more than one diisocyanate selected from the group consisting of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-methylenediphenyl diisocyanate, 2,4,6-trimethyl-1,3-phenylene diisocyanate, ~~2,3,4,5~~2,3,5,6-tetramethyl-1,4-phenylene diisocyanate,

b) annealing the membrane from step a) at 280 to the glass transition temperature of the polymer, about 360-370°C,

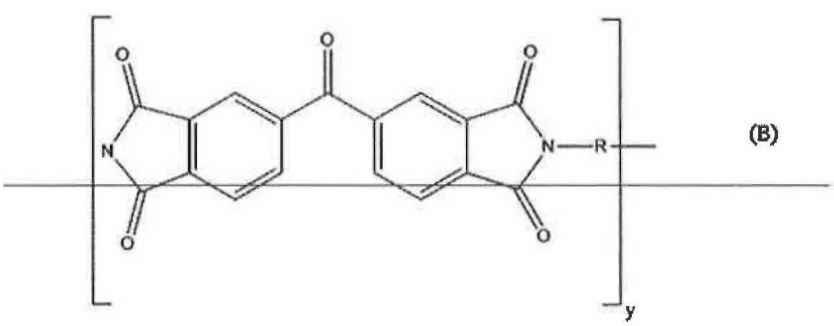
and is characterized in that

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.

The polyimide in step a) is preferably a polyimide consisting of monomer units (A) and (B), wherein ~~of the following~~ composition:



(A)



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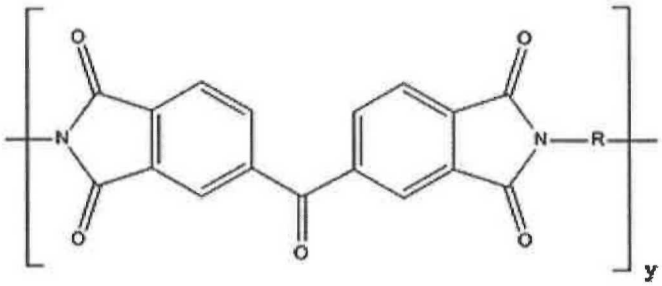

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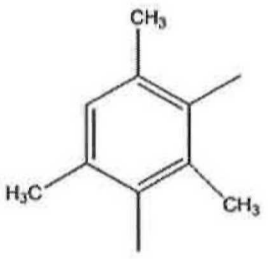
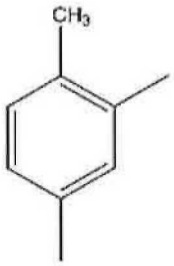
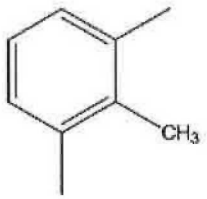


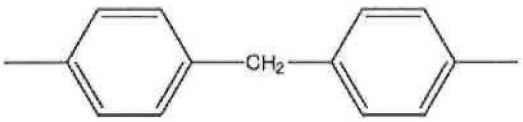
(L1)



(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.

The polyimide is very particularly preferably a polymer where ~~X~~x = 0, ~~Y~~y = 1 and R consists of 64 mol% L2, 16 mol% L3 and 20 mol% L4. This polymer is commercially available under the name P84 or P84 type 70 and has the following CAS number: 9046-51-9. The specific preference in stage a) is for a polymer having the composition x = 0.4, y = 0.6 and R consists of 80 mol% L2 and 20 mol% L3. This polymer is commercially available under the name P84HT or P84 HT 325 and has the following CAS number: 134119-41-8.

The annealing conditions can be varied according to the property desired for the membranes. Membranes having a very good gas selectivity are obtained starting at a temperature of 280°C. At temperatures of more than 280°C in the case of P84 type 70 and above 300°C in the case of P84 HT, moreover, the molecular weight becomes stabilized, so the molecular weight stability can be established at these temperatures. In addition to the annealing temperature, the duration of the annealing step can also be used to influence the selectivity and the molecular weight stability. Without wishing to be tied to any one theory, the inventors believe that annealing the dried membrane causes the membrane structure to

longer cause any damage. Whether the annealing operation was successful, i.e. no undesired oxidation took place, is *inter alia* also ascertainable from the fact that the membrane has no visible (slightly orange) discoloration. Undesired oxidation can also be ascertained using FT-IR.

Cooling the membranes after annealing can be "passive", i.e. by switching off the heat source. However, it is particularly preferable for the membranes which have been completely annealed to be cooled down "actively", for example by flushing the oven or contacting the membrane with an appropriately temperature-regulated inert gas having the hereinbelow specified O_2 content. Alternatively, however, it is likewise preferable to cool with a heat exchanger and/or a cooling circuit. Further technical modulations to effectuate appropriate cooling are known to one skilled in the art and are encompassed by the present invention. Active cooling enhances the space-time yield and reduces the risk of yet still incurring an undesirable deterioration in membrane properties during cooling.

Step a) according to the invention can in principle be carried out according to any desired method of producing polyimide membranes. However, methods leading to membranes having a nanoporous structure are particularly preferred. When the membranes produced as a starting material for step b) already have a fairly thick separating layer or a dense structure, the anneal will effect a further improvement in their selectivity and prevent molecular weight degradation, but will also have the effect that the membranes are still further densified and thus a very thick separating layer is obtained. This in turn has the consequence that, although the membranes do have very good selectivity, they also have poor permeance and thus poor productivity. The effectivity of the method according to the present invention can thus be still further increased by producing in step a) a membrane which is characterized by a correspondingly high permeance. Permeance is a measure of the gas flux and thus an indicator of the structure of the membrane. The membranes produced in step a) of the method according to the present invention thus preferably have an O_2 permeance of not less than 25 GPU (Gas Permeation Unit, 10^{-6} $cm^3.cm^{-2}.s^{-1}.cmHg^{-1}$), 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. Corresponding membranes are preferably obtainable by the methods described hereinbelow.

In a first preferred embodiment, the membrane production process comprises in step a) the following sub-steps:

a1) polymerization

a2) producing the casting solution

a3) membrane production

a1) Polymerization

The polyimides used according to the present invention are produced via a polycondensation of one or more of the abovementioned aromatic tetracarboxylic dianhydrides with one or more of the abovementioned aromatic diisocyanates by release of carbon dioxide.

The polymerization is preferably carried out in an aprotic dipolar solvent. Preferably but not exclusively, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, N-ethylpyrrolidone and sulpholane are used, singly or in mixtures.

This preferably involves the aromatic dianhydride or mixtures of aromatic dianhydrides being dissolved in concentrations of 10% by weight to 40% by weight, preferably between 18% by weight and 32% by weight and more preferably between 22% by weight and 28% by weight in an aprotic dipolar solvent and heated to from 50°C to 150°C, preferably 70°C to 120°C and more preferably to from 80°C to 100°C. This solution is admixed with 0.01% by weight to 5% by weight, preferably 0.05% by weight to 1% by weight and more preferably 0.1% by weight to 0.3% by weight of a basic catalyst. Useful catalysts include:

- Alkali or alkaline earth metal hydroxides, methoxides, ethoxides, carbonates and phosphates such as for example but not exclusively sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, sodium ethoxide, potassium ethoxide, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, potassium phosphate, potassium hydrogenphosphate, potassium dihydrogenphosphate
- Tertiary amines such as for example but not exclusively: trimethylamine, triethylamine, tripropylamine, diazabicycloundecane, diazabicyclooctane, dimethylaminopyridine.

the pore size is influenced by the species of volatile solvent, its concentration, the evaporation time, the casting solution temperature, the amount and temperature of ambient gas in the evaporative removal zone.

Useful volatile solvents include the following. They should be water miscible, for example acetone, tetrahydrofuran, methanol, ethanol, propanol, isopropanol, dioxane~~, diethyl ether~~.

Producing the casting solution is preferably effected by adding additives by metered addition of the mixture of additives or separately from each other in succession. The additives are preferably gradually metered into the mixture under agitation. The metered addition takes between 10 min and 3 hours for preference and between 30 min and 2 hours for particular preference. Adding the cosolvents causes partial precipitation of polyimide at the drop entry point. But the solids dissolve again after a few minutes without leaving a residue. The clear solution is then preferably additionally filtered through a steel mesh sieve, more preferably of about 15 µm mesh width, in order to remove destructive concomitants which would lead to imperfections in the membrane surface.

After filtration, the solution is preferably devolatilized and freed of air bubbles. This is generally done by applying a negative pressure via a vacuum pump.

a3) Producing the hollow fibres

The devolatilized, filtered and optionally additized casting solution is preferably thermostated – preferably to from 20 to 100°C and more preferably to from 30 to 70°C. The solution is then gear pumped, for example, through the outer part of a two-material die. The external diameter of the two-material die is preferably in the range from 500 to 800 µm, more preferably in the range from 550 to 750 µm, the internal diameter is preferably in the range from 200 to 400 µm, more preferably from 250 to 350 µm, and pump rate is preferably between 0.1 and 13.5 ml/min. A liquid mixture of water and one or more than one aprotic dipolar solvent in admixture is pumped in the inner part of the two-material die as bore solution.

Useful aprotic dipolar solvents include *inter alia* but not exclusively dimethylformamide, dimethylacetamide, N-methylpyrrolidone, N-ethylpyrrolidone, sulpholane or dimethyl

particularly preferable to heat the water baths to 40-90°C, preferably 50-80°C, to achieve a more effective wash.

However, it is also possible for the fibres obtained from the precipitation bath to be wound up on a bobbin and be washed in water off-line. The wash can take place at any temperature. Preferably, however, comparatively high temperatures are used for the wash as described above. It is preferable to direct the water in cross-flow along the fibres, i.e. to force it from the inside surface of the bobbin to the outside.

This is preferably followed by a solvent exchange, more preferably in isopropanol and/or hexane, to remove water and dimethylformamide (DMF). The solvent exchange can be carried out as a continuous operation (on-line) or off-line, like the wash. For an on-line solvent exchange, the fibres are led through one or more solvent baths, preferably downstream of the wash bath(s).

The fibres are then dried – preferably at a temperature in the range from room temperature and 150°C, more preferably between 50 and 100°C, removing isopropanol and hexane. The overall water and/or residual solvent content after drying is in the range from 0% to 5% by weight, preferably <3% by weight and more preferably in the range from 0.1% to 3% by weight, and preferably consists of the water, isopropanol and hexane fractions. It has transpired that a low residual solvent and water content offers additional advantages for the anneal. As shown in Comparative Example 4, an excessively high residual content level of water and solvent in the annealing of entire membrane bundles causes the membranes to stick together. Therefore, it is not possible for entire membrane bundles to be annealed when the residual content is too high. Instead, the membranes would have to be annealed individually at additional expense and inconvenience. There is moreover a risk with this of resultant inhomogeneities in the membrane bundle due to variations with the annealing of individual membranes. As shown in Comparative Example 4, the short drying in EP 0321569 is completely insufficient in that the membrane bundle became stuck together.

Too much water can further lead to hydrolysis and hence chain scissioning and thus to a mechanically unstable membrane. Although some of the water and some of the solvent will evaporate during annealing, it has been determined that the maximum content before commencement of annealing is advantageously below 5% by weight, preferably below 3% by weight.

- the polyimide is a polyimide comprising

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, 2,3,4,6-trimethyl-1,3-phenylene diisocyanate, ~~2,3,4,5~~2,3,5,6-tetramethyl-1,4-phenylene diisocyanate,

and in that

- the level of extraneous and crosslinking substances in the membrane is in the range from 0% to 5% by weight, preferably 0% to 1% by weight,
- they have a solubility in DMF of 5 to 95%, preferably 5 to 90%, more preferably 10 to 80% and still more preferably 20 to 70%

and

- they have a layer thickness of the actual separating layer of not more than 1.5 µm, preferably not more than 1 µm, more preferably not more than 750, still more preferably not more than 500 nm, yet still more preferably not more than 250 nm and yet still even more preferably not more than 100 nm.

The polyimide is preferably a polyimide disclosed as preferable above in the description of the production method.

As mentioned, the method of the present invention is the first successful way of providing membranes combining very high gas selectivity with very good productivity and a high molecular weight stability under thermal stress. The membranes annealed according to the present invention can be varied in DMF solubility by means of the method according to the

After effected analysis, the residual solvent content is automatically computed according to the formula

$$\frac{\text{area}}{\text{cal.curve} \cdot \text{initial weight [mg]}} \cdot 100 = \text{residual solvent (\%)}$$

and printed out under "Concentration [%]".

Determination of residual water content

Residual water content is determined by extracting the membranes with isopropanol and a subsequent analysis by Karl Fischer titration. The membranes are transferred into a previously dried 250 ml Schott glass and covered with a weighed-out amount of dry isopropanol up to the top. The container is left to stand at room temperature overnight.

Production examples

The examples which follow serve to provide more particular elucidation and better understanding of the present invention, but do not limit it in any way.

Example 1

To produce the spinning solution, a 3 l glass flask equipped with a stirrer and reflux condensers was initially charged with 1800 g of anhydrous dimethylformamide. 316.4 g of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 142.8 g of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) were dissolved therein and the solution was heated to 80°C. 1.8 g of diazabicyclooctane were added to this solution. Under nitrogen, 283.4 g of a mixture of 80% 2,4-tolylene diisocyanate and 20% 2,6-tolylene diisocyanate are metered in during several hours. In the process, CO_2 escaped as a by-product and a polyimide is obtained directly in solution.

The resultant 27% by weight spinning solution in DMF was then devolatilized, thermostated to 50°C and gear pumped through a two-material die. The flow rate was 324 g/h. While the polymer solution was conveyed in the outer region of the two-material die, a mixture of 70% dimethylformamide and 30% of water was conveyed as bore solution in the inner region in order to produce the hole in the hollow fibres. The flow rate of the bore solution was 120 ml/h. After a distance of 13 cm from the die, the hollow fibre entered warm water at 50°C. The hollow fibre travelled through a tube on the way from the die to the precipitation bath. This tube was flooded with a 1 l/min stream of nitrogen, tube internal temperature was

To produce polyimide solution 1 in DMF, a 3 l glass flask equipped with a stirrer and reflux condensers was initially charged with 1622 g of anhydrous dimethylformamide. 456.4 g of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride were dissolved therein and the solution was heated to 85°C. 0.45 g of comminuted sodium hydroxide were added to this solution. Under nitrogen, 266.8 g of a mixture of 80% 2,4-tolylene diisocyanate and/or 2,6-tolylene diisocyanate and 20% 4,4'-diphenylmethane diisocyanate are metered in during several hours. In the process, CO_2 escaped as a by-product and a polyimide is obtained directly in solution.

To produce polyimide solution 2 in DMF, a 3 l glass flask equipped with a stirrer and reflux condensers was initially charged with 1800 g of anhydrous dimethylformamide. 316.4 g of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 142.8 g of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) were dissolved therein and the solution was heated to 80°C. 1.8 g of diazabicyclooctane are added to this solution. Under nitrogen, 283.4 g of a mixture of 80% 2,4-tolylene diisocyanate and 20% 2,6-tolylene diisocyanate are metered in during several hours. In the process, CO_2 escaped as a by-product and a polyimide is obtained directly in solution.

The polyimide solutions were mixed together in a cat can and homogenized on a rollstand over the weekend. This gave a bulk viscosity of 79 Pas at 25°C and a solids content of 27.8%.

The casting solution thus obtained was devolatilized, thermostated to 50°C and gear pumped through a two-material die. The flow rate was 324 g/h. While the polymer solution was conveyed in the outer region of the two-material die, a mixture of 70% dimethylformamide and 30% of water was conveyed as bore solution in the inner region in order to produce the hole in the hollow fibres. The flow rate of the bore solution was 120 ml/h. After a distance of 13 cm from the die, the hollow fibre entered warm water at 50°C. The hollow fibre travelled through a tube on the way from the die to the precipitation bath. This tube was flooded with a 1 l/min stream of nitrogen, tube internal temperature was 35°C.The fibre was hauled through the water wash bath and finally wound up at a speed of 50 m/min. After extraction with water for several hours, the hollow fibres were dipped into isopropanol and thereafter dried at 70°C in a drying zone. The membranes obtained contain less than 2% by weight of water, ≤ 0.5% by weight of residual solvent (isopropanol, hexane) and 0.1% by weight of residual DMF, and were heated at a rate of 2°C/min to 310°C in N_2 (O_2 content of 0.001%) and subsequently left at the final temperature for 1 h.

Claims

1) A method of producing polyimide membranes,

~~characterized in that~~ wherein ~~it~~ 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, ~~2,3,4,5~~2,3,5,6-tetramethyl-1,4-phenylene diisocyanate,

b) annealing the membrane at a temperature in the range from 280 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,

~~characterized in that~~ wherein

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,

~~characterized in that~~ wherein

the anneal is conducted for 15 to 300 min, preferably for 30 to 240 min, more preferably for 60 to 120 min and still more preferably for 60 to 90 min from the time at which the target temperature for the anneal is attained,

and/or ~~in that~~ 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 ~~in that~~ 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 ~~in that~~ 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 ~~and~~or 2,

~~characterized in that~~ 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) ~~or before step a1)~~ 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,
~~characterized in that~~ 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 ~~in that~~ 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 ~~diethyl ether,~~ 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 ~~and~~ or 2,

~~characterized in that~~ 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,

~~characterized in that~~ 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 ~~in that~~ 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,

~~characterized in that~~ 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,

~~characterized in that~~ 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~~, more preferably~~ 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,

~~characterized in that~~ wherein

the gas or gas stream used is nitrogen, air, argon, helium, carbon dioxide, methane or other industrial inert gases or mixtures thereof,

and/or ~~in that~~ 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,

~~characterized in that~~ 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 ~~in that~~ wherein

the membranes were subjected to a solvent exchange before the anneal, but preferably after the wash,

and/or ~~in that~~ 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 ~~drying~~ annealing step,

and/or ~~in that~~ wherein

the membrane haul-off speed is 10 and 80 m/min, preferably between 30 and 70 m/min,

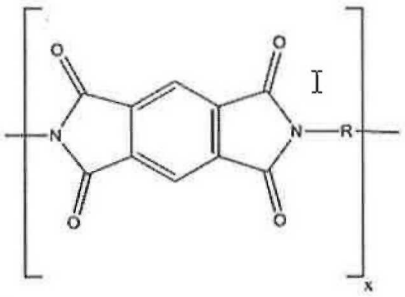
and/or ~~in that~~ wherein

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

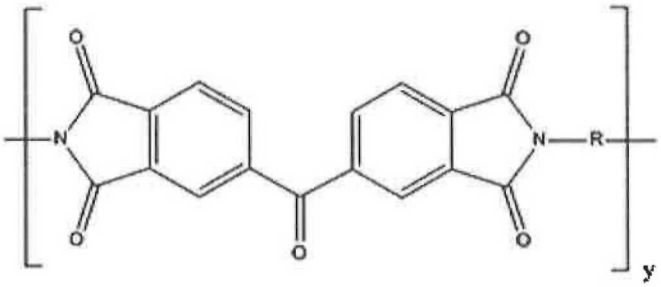
2000 GPU, still more preferably from 200 to 1500 GPU, yet still more preferably from 300 to 1000 GPU and yet still even more preferably from 400 to 800 GPU.

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)



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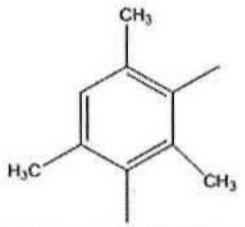
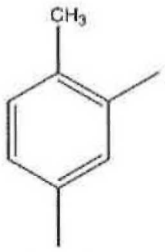
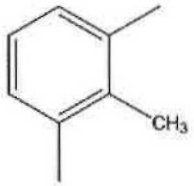


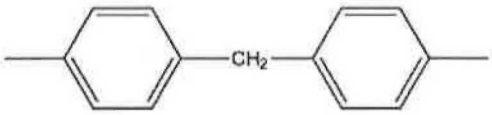
(L1)



(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, 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.

~~11)~~12) A polyimide membrane

~~characterized in that~~ wherein

- the polyimide is a polyimide comprising

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, 2,3,4,52,3,5,6-tetramethyl-1,4-phenylene diisocyanate,

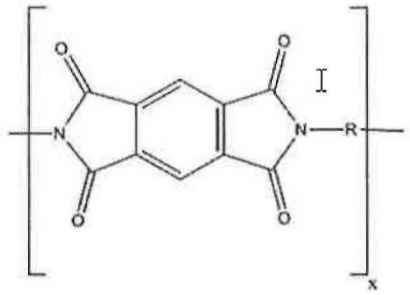
- the level of extraneous and crosslinking substances in the membrane is in the range from 0% to 5% by weight, preferably 0% to 1% by weight,
- it has a solubility in DMF of 5 to 95%, preferably 5 to 90%, more preferably 10 to 80% and still more preferably 20 to 70%

and

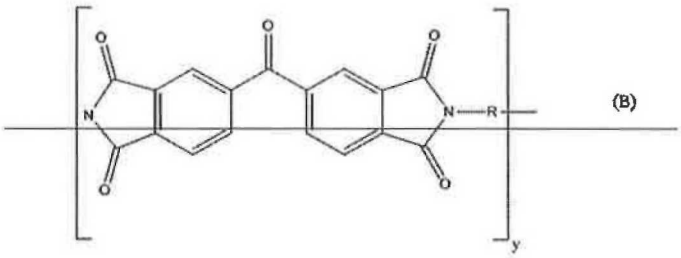
- it has a layer thickness of the actual separating layer of not more than 1.5 µm, preferably not more than 1 µm, more preferably not more than 750, still more preferably not more than 500 nm, yet still more preferably not more than 250 nm and yet still even more preferably not more than 100 nm.

12)13) The polyimide membrane according to Claim 121 or a method according to any one of Claims 1 to 10, characterized in that wherein

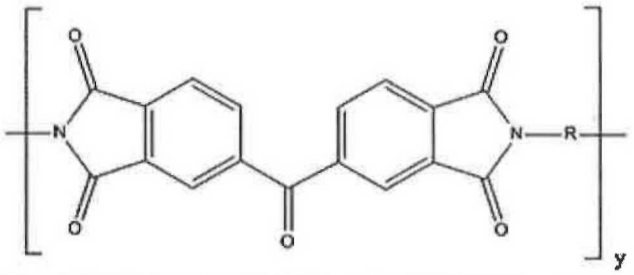
the polyimide is a polyimide consisting of monomer units (A) and (B), and wherein of the following composition:



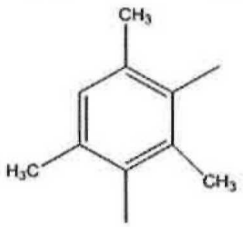
(A)



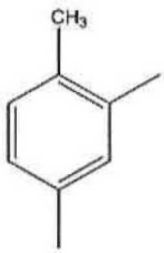
(B)



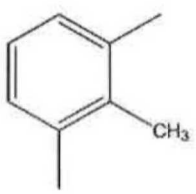
(B)



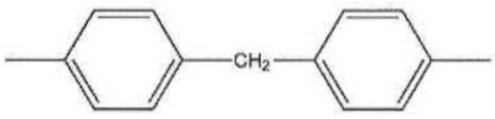
(L1)



(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, preferably in that the polyimide is a polymer where ~~X~~x = 0, ~~Y~~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.

~~13)~~14) Polyimide membranes according to either ~~any one~~ of Claims ~~10 to 12~~12 or 13, ~~characterized in that~~ wherein
the polyimide membranes are

integrally asymmetric flat sheet membranes on a backing fleece, preferably a backing fleece of polyphenylene sulphide, polyethylene terephthalate or polypropylene,

or integrally asymmetrical hollow fibre membranes.

~~14) A polyimide membrane obtainable according to any one of Claims 1 to 10.~~

15) The use of polyimide hollow fibre membranes according to any one of Claims ~~10~~12 to 14 for separating gas mixtures, preferably

for separating methane and carbon dioxide,

~~and/~~or

for separating oxygen and nitrogen,

~~and/~~or

for separating hydrogen from process gases,

~~and/~~or

for separating water vapour ~~and/~~or helium from gases or gas mixtures.