(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2012 (27.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/177133 A1

(51) International Patent Classification:
B01D 71/64 (2006.01) *B01D 69/02* (2006.01)
B01D 67/00 (2006.01)

(21) International Application Number:
PCT/NL2012/050440

(22) International Filing Date:
22 June 2012 (22.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11171318.6	24 June 2011 (24.06.2011)	EP
61/500,732	24 June 2011 (24.06.2011)	US

(71) Applicants *(for all designated States except US)*: **Stichting voor de Technische Wetenschappen** [NL/NL]; Van Vollenhovenlaan 661, NL-3527 JP Utrecht (NL). **Universiteit Twente** [NL/NL]; Drienerlolaan 5, NL-7522 NB Enschede (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **Dutczak, Szymon Maria** [PL/DE]; Viefhoek 6, 48565 Steinfurt (DE). **Cuperus, Folkert Petrus** [NL/NL]; Vlietweg 81, NL-7335 JE Apeldoorn (NL). **Stamatialis, Dimitrios** [GR/NL]; Pijlkruidlaan 14, NL-7534 JJ Enschede (NL).

(74) Agent: **de Boer, Henk**; J.W. Frisolaan 13, NL-2517 JS The Hague (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2012/177133 A1

(54) **Title**: CROSS-LINKED POLYIMIDE MEMBRANES

(57) **Abstract**: The present invention relates to a process for cross-linking a membrane comprising a polyimide, wherein the polyimide is cross-linked with a cross-linking agent comprising two or more isocyanate groups. The present invention also relates to a membrane obtainable by this process and to the use of the membrane in a separation process. The present invention also relates to a process for separating a dissolved component having a molecular weight of about 100 to about10000 Dalton from a solution, said process comprising: (a) contacting the solution with the membrane, and (b) isolating or concentrating the component.

Cross-linked polyimide membranes

Field of the invention

The present invention relates to a process for cross-linking a membrane comprising a polyimide, wherein the polyimide is cross-linked with a cross-linking agent. The present invention also relates to a membrane comprising a cross-linked polyimide and the use of such a membrane in separation processes.

Background of the invention

Membrane filtration is a separation process that utilizes membranes to discriminate between components on the basis of differences in size, affinity, molecular weight and the like. The ability of the membrane to separate is usually expressed by the molecular weight cut-off (MWCO) which is defined as a molecular weight of a component that is rejected for 90 % by the membrane. Membrane filtration processes include microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In membranes used for nanofiltration (NF), the MWCO is commonly 200 - 2000 Dalton (Da or g/mole).

In water purification, membrane technology is a widely spread and accepted technology. Despite the fact, that membrane filtration is an energy-efficient separation process with high potential in many industries ranging from petro-chemistry to pharmaceutical industry and waste treatment, it has not been widely applied for separations in organic solvents, yet. This is mainly due to the interaction of the membrane material (especially polymeric ones) with the solvent and the solute which renders them less effective and in many cases not even selective. Moreover, for separations in apolar, aprotic organic solvents such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF) or dimethyl acetamide (DMA), which themselves are solvents for polymeric materials and often used for membrane fabrication, there are hardly polymeric nanofiltration membranes available today.

During separation in such systems, the polymeric membranes often suffer excessive swelling or even complete dissolve in the organic solvent. Consequently, the membrane selectivity decreases and the membrane become useless. Modifying polymeric membranes to improve their resistance to organic solvents has been done by cross-linking.

US 4.075.093, incorporated by reference, discloses a process for separating citric acid, isocitric acid, salts thereof, and mixtures thereof, from an aqueous solution, wherein the aqueous solution is contacted with a permselective membrane comprising a polymer having acidic groups or a polymer having basic groups. The membrane is preferably a polyimide or a polyamide modified with acidic or basic groups. Example 8 discloses the synthesis of a polyimide containing amino groups, which is prepared by reacting the polyimide membrane of Example 2 (a sulfonated polyimide membrane) with 4,4-diphenylmethane di-isocyanate (MDI) in DMF at 100°C.

H. Deligöz *et al.*, Eur. Polym. J. *42*, 1370 - 1377, **2006**, incorporated by reference, discloses cross-linked polyimide films that have been prepared in three steps: (1) reaction of diaminodiphenyl ether with pyromellitic dianhydride to obtain a poly(amic acid) intermediate (PAA), (2) reaction of a solution of PAA in NMP with a solution of an equivalent amount of 4,4-diphenylmethane di-isocyanate (MDI) as a cross-linker in the solvent NMP to prepare a PAA gel and (3) preparation of a cross-linked polyimide film by thermal imidization of the PAA gel.

V.A. Bershtein *et al.*, Polymer *43*, 6943 - 6953, **2002**, discloses poly(imide-amide)-poly(ethylene adipate) hydrid networks (PIA-PEA networks). Films are prepared by casting a solution of (a) polyamic acid (PAA) based on pyromellitic dianhydride (PMDA) with oxydianiline (ODA) in NMP and a solution of (b) toluene-2,4-di-isocyanate (TDI) terminated poly(ethylene adipate) (TDI-PEA), wherein the remaining isocyanate groups were end-capped with phenol, i.e. the compound abbreviated as [Ph-TDI-PEA], in NMP on a glass plate. After evaporation of the solvent (NMP), the films were subjected to a heat treatment, wherein the isocyanate groups are deprotected, so that the PAA imidization and the cross-linking reaction proceed in parallel.

US 2010/0038306, US 2010/0181253 and WO 2010/142979, all incorporated by reference, disclose a process for cross-linking polyimide membranes with low molecular weight diamines, e.g. 1,2-diamino ethane and 1,6-hexane diamine, and high

molecular weight diamines, e.g. polyether amines having a molecular weight of 200 to 200.000 and polyethylene amines having a molecular weight of 1000 to 200.000. It is preferred that the low molecular weight diamines are dissolved in a solvent selected from the group consisting of ketones, ethers and alcohols. More preferably, the solvent is an alcohol, most preferably methanol or ethanol, which are polar protic solvents. However, the cross-linked polyimide membranes obtained in this manner do not appear to be stable at elevated temperatures. For example, at temperatures above about 100°C, re-imidization may occur leading to decreased solvent resistance. Moreover, the diamines used in the process may not be used at too high concentrations and the cross-linking reaction should not occur for long time as otherwise dissolution or degradation of the membrane may occur.

US 2009/0069507 discloses blends of aromatic polyimides and polyarylenes, wherein the aromatic polyimides comprise an aromatic ring and an imide group. The polyimide may be a polyamide-imide such as Torlon® polyamide-imides.

The present invention provides a solution for these problems and provides membranes which are resistant to organic solvents and which can be used in separation processes at elevated temperature, in particular above about 100°C.

Summary of the invention

The present invention relates to a process for cross-linking a membrane comprising a polyimide, wherein the polyimide is cross-linked with a cross-linking agent comprising two or more isocyanate groups.

The present invention further relates to a membrane comprising a cross-linked polyimide.

The present invention also relates to the use of a membrane comprising a cross-linked polyimide in a separation process as a support in a separation process, wherein the membrane comprises a selective top layer.

The present invention further relates to a process for separating a dissolved component having a molecular weight of about 100 to about 10000 Dalton from a solution, said process comprising:

(a) contacting the solution with a membrane comprising the cross-linked polyimide; and

(b) isolating or concentrating the component.

Detailed description of the invention

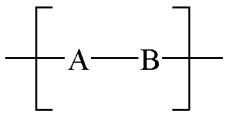
The verb “to comprise” as is used in this description and in the claims and its conjugations is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there is one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

In this document, the term “separation process” must be understood as encompassing processes such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and pervaporation. Such processes are well known in the art.

In this document, the term “polyimides” must be understood as polymers or copolymers comprising an amide group (-NR*-C(O)-) and/or an imide group (-(C(O)-NR*-C(O)-), wherein R* represents hydrogen or an optionally substituted hydrocarbyl group, the hydrocarbyl group being optionally a polymeric residue). Hence, the term “polyimides” includes polymers known as “polyamide-imides”.

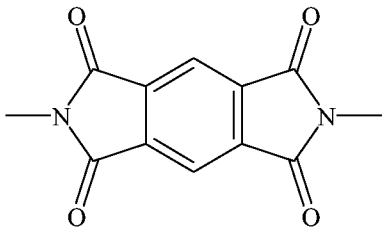
The polyimide

According to the invention, the polyimide is preferably a polyimide according to Formula (1):

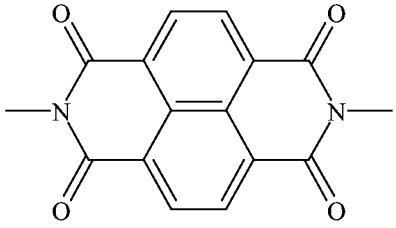


(1)

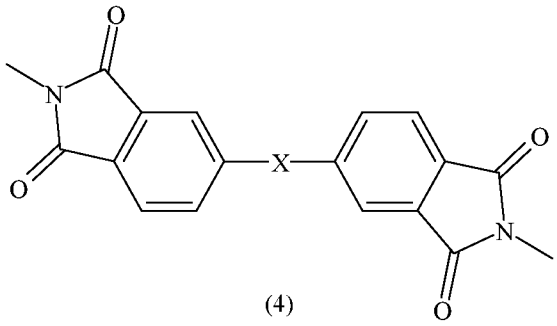
wherein recurring unit A is independently selected from the group consisting of the structures according to Formulas (2) - (4):



(2)



(3)



(4)

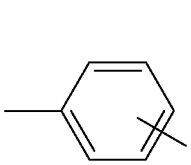
wherein X:

(a) is absent (so that the two aryl groups are connected via a direct bond);

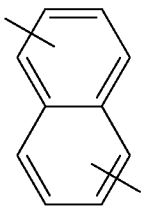
(b) -C(O)-; and

(c) $-(CR^1_2)_n-$, wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5;

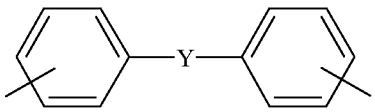
wherein recurring unit B is independently selected from the group consisting of the structures according to Formulas (5) - (8):



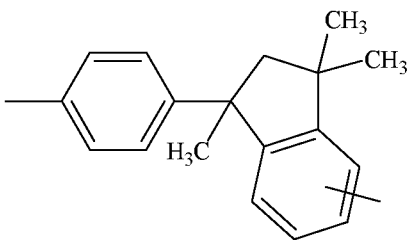
(5)



(6)



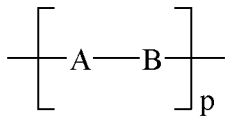
(7)



(8)

wherein Y is independently selected from the group consisting of -C(O)-, -$(CR^1_2)_n$-, -O-, -S-; -S(O)-, and -$S(O)_2$-; wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5.

Preferably, the polyimide is a polyimide according to Formula (1a):



(1a)

wherein p is such that the molecular weight of the polyimide is about 10.000 to about 1.000.000 Dalton, preferably about 20.000 to about 500.000 Dalton.

The polyimides according to Formula (1) and Formula (1a) are commercially available from for example Solvay Advanced Polymers (Torlon®), Huntsman (Matrimid®) and Evonik Industries (P84®).

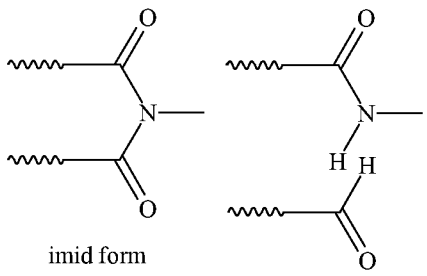
The structures according to Formulas (2) - (8) encompass also the tautomers thereof.

According to a preferred embodiment, the recurring unit A is of Formula (4), wherein it is preferred that X is -C(O)-.

According to a preferred embodiment of the present invention, the recurring unit B is of Formula (7) or (8).

According to another preferred embodiment, the recurring unit B is of Formula (7) or (8), wherein it is preferred that Y is -$(CR^1_2)_n$- or O. When Y is -$(CR^1_2)_n$-, it is preferred that n is 1. It is also preferred that R^1 is H.

As will be understood by the skilled person, the imide groups in recurring unit A may occur in the corresponding amic acid form:



The cross-linking agent

In a preferred embodiment, the cross-linking agent comprises two or more isocyanate groups, preferably two or three isocyanate groups.

According to the present invention, it is more preferred that the cross-linking agent is selected from the group consisting of optionally substituted C_1 - C_{20} alkylene diisocyanates and optionally substituted C_6 - C_{20} arylene diisocyanates, wherein the alkylene group may be linear, cyclic or branched. It is preferred that the alkylene group is linear.

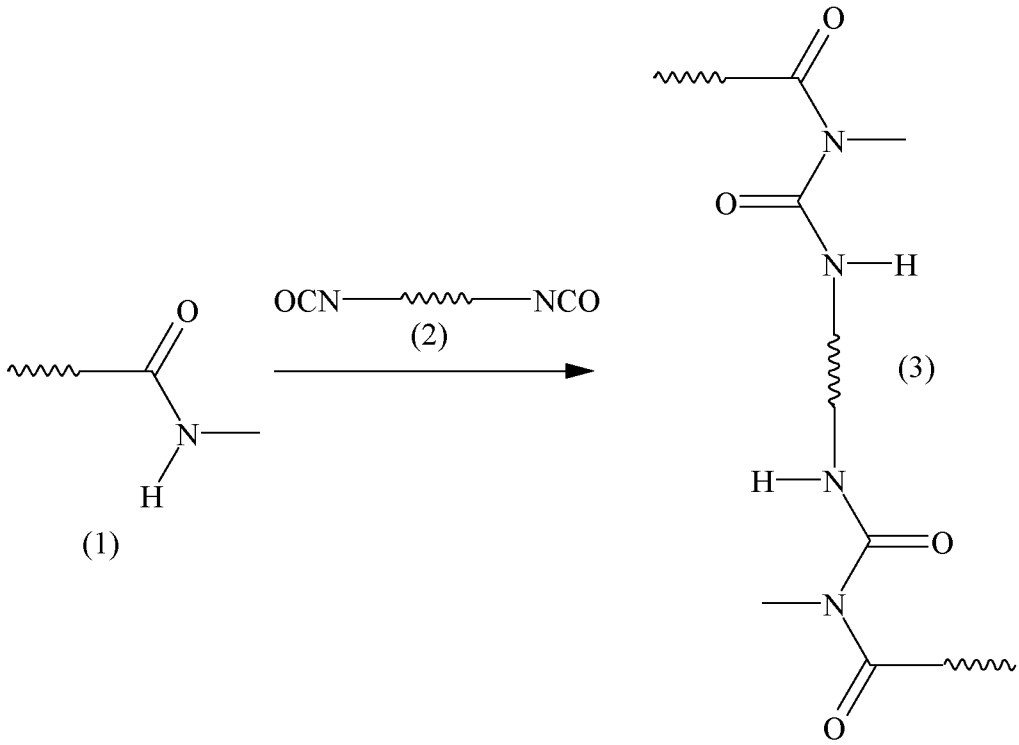
Preferably, the optionally substituted C_1 - C_{20} alkylene diisocyanates are selected from the group consisting of 1,3-trimethylene diisocyanate, 1,4-tetramethylene diisocynanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-hexane diisocyanate, 2,4,4-trimethyl-hexane diisocyanate, isophoronediisocyanate, and 4,4′-methylenebis(cyclohexyl isocyanate). More preferably, the optionally substituted C_1 - C_{20} alkylene diisocyanates are selected from the group consisting of 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-hexane diisocyanate, 2,4,4-trimethyl-hexane diisocyanate and isophoronediisocyanate.

The optionally substituted C_6 - C_{20} arylene diisocyanate is preferably 4,4'-methylene bis(phenyl isocyanate).

The cross-linking reaction

According to the present invention, the cross-linking reaction of the polyimide proceeds according to the general Scheme 1:

Scheme 1



wherein structure (1) represents the polyimide, structure (2) represents the cross-linking agent comprising two or more isocyanate groups, and structure (3) represents the cross-linked polyimide.

Preferably, the process is performed in a solvent system which is an aprotic solvent and does not dissolve the membrane. Such solvent systems swell the membrane and allow diffusion of the cross-linking agent into the polymer matrix of the membrane. It is preferred that the solvent system comprises a polar, aprotic solvent which is a solvent for the polyimide, and a polar, aprotic solvent which is a non-solvent for the polyimide, provided that the solvent systems comprises the solvent for the polyimide and the non-solvent for the polyimide in such a ratio that the polyimide swells but essentially does not dissolve. It is also preferred that the polar, aprotic solvent has a dielectric constant ε of at least 2 at 20°C. Suitable solvents can be selected by from e.g. CRC Handbook of Chemistry & Physics, 59th Ed., 1978 - 1979. More

preferably, the solvent for polyimide is selected from the group consisting of NMP (N-methyl pyrrolidone; ε = 32.2), DMSO (dimethyl sulfoxide; ε = 46.7), DMA (dimethyl acetamide; ε = 37.8), DMF (dimethylformamide; ε = 36.7) and γ-butyrolactone (ε = 42.4.). The given values for ε are for 20°C.

Preferably the non-solvent is an ether, ketone or halogenated hydrocarbon. More preferably the non-solvent is selected from the group consisting of dioxane (ε = 2.25), cyclopentanone (ε = 2.3) and cyclohexanone (ε = 18.3) and THF (tetrahydrofuran; ε = 7.58).

According to an embodiment of the present invention, the non-solvent for the polyimide is optionally in admixture with a solvent for the polyimide, preferably at a ratio (w/w) of about 99/1 to about 70/30, more preferably about 99/1 to about 15/85.

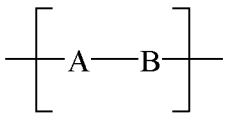
The cross-linking reaction may be performed in the presence of a catalyst, preferably a tertiary amine, N-C_1-C_6 alkyl substituted 2-pyrrolidinone such as NMP, pyridine, oxazole and a co-catalyst or a mixture of such catalysts. It is preferred that the catalyst is a tertiary amine or a N-C_1-C_6 alkyl substituted 2-pyrrolidinone. Even more preferred, the catalyst is selected from the group consisting of triethylene diamine (TEDA), bis(2-dimethylaminoethyl)ether (BDMAEE), N-ethylmorpholine, N'N'-dimethylpiperazine, N,N,N',N',N''-pentamethyl-diethylene-triamine (PMDETA), N,N-dimethylcyclohexylamine (DMCHA), N,N-dimethylbenzylamine (DMBA), N,N-dimethylcethylamine, N,N,N',N",N"-pentamethyl-diproylene-triamine (PMDPTA), Tritethylamine (TEA). It is even more preferred that the catalyst is 1-Methyl-2-pyrrolidinone (NMP) and /or Triethylamine (TEA).

It is preferred that the co-catalyst is an alkaline metal salt such as potassium carbonate, sodium carbonate, sodium hydrogen carbonate, Potassium acetate, Potassium octoate and calcium carbonate or an organometallic compound. It is more preferred that the co-catalyst is an organometallic compound containing selected from the group of tin 2-ethylhexanoate, dibutyltin dilaurate (DBTL), dibutyltin mercaptide, dibutyltin thiocarboxylates, phenylmercuric propionate, lead octoate, ferric acetylacetonate. It is even more preferred that the co-catalyst is tin 2-ethylhexanoate, dibutyltin dilaurate and lead octoate.

The cross-linked polyimide membrane

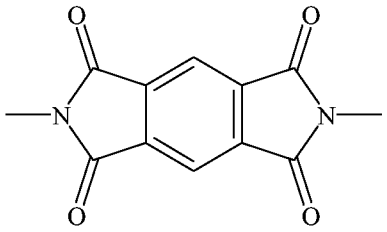
The present invention also relates to a cross-linked polyimide membrane that is obtainable by the process according to the present invention. Preferably, the cross-linked membrane has a MWCO of about 100 to about 10000 Dalton, more preferably of about 100 to about 6000 Dalton, even more preferably of about 100 to about 2000 and in particular of about 200 to about 2000.

The present invention therefore also relates to a cross-linked membrane comprising a polyimide according to Formula (1):

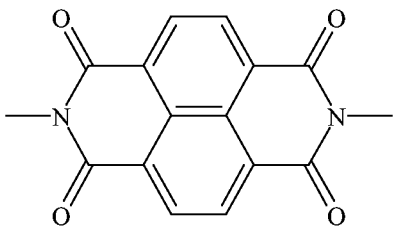


(1)

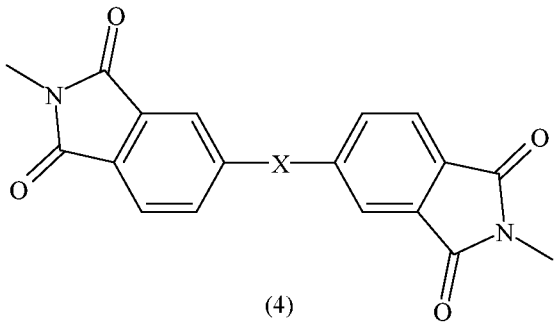
wherein recurring unit A is independently selected from the group consisting of the structures according to Formulas (2) - (4):



(2)



(3)



(4)

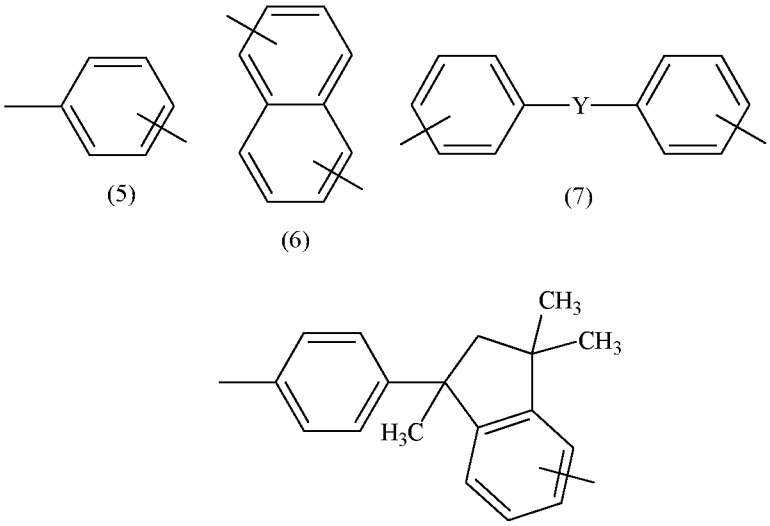
wherein X:

(a) is absent (so that the two aryl groups are connected via a direct bond);

(b) -C(O)-; and

(c) $-(CR^1_2)_n-$, wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5;

wherein recurring unit B is independently selected from the group consisting of the structures according to Formulas (5) - (8):



(5) (6) (7) (8)

wherein Y is independently selected from the group consisting of -C(O)-, $-(CR^1_2)_n-$, -O-, -S-; -S(O)-, and $-S(O)_2-$; wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5; and wherein the imide groups, optionally in their amic acid form, in recurring unit A are cross-linked with a cross-linking agent comprising two or more isocyanate groups.

Applications

The cross-linked membrane according to the present invention can in particular be used in a separation process. Preferably, the separation process is a membrane filtration processes which preferably is either a pervaporation, microfiltration, an ultrafiltration, a nanofiltration or a reverse osmosis, or a combination thereof.

Preferably, the membrane separation process comprises the application of a solvent for a non-crosslinked polyimide.

According to another embodiment of the present invention, the membrane can also be used as a support in a pervaporation, nanofiltration or reverse osmosis process, wherein the membrane comprises a selective top layer.

Accordingly, the present invention also relates to a process for separating a dissolved component having a molecular weight of about 100 to about 10000 Dalton from a solution, said process comprising:

(a) contacting the solution with a membrane according to the invention; and

(b) isolating or concentrating the component.

Preferably, this process is performed under a pressure of about 0.1 kPa to about 5 MPa, more preferably about 10 kPa to about 4 MPa, and even more preferably about 100 kPa to about 4 MPa.

Preferably, this process is performed at a temperature of about -10° to about 200 °C, more preferably about 0° to about 150°C.

Preferably, this process is performed in an organic solvent. Preferably, the solvent is a strong aprotic solvent and is preferably be selected from the group consisting of N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl acetamide (DMA), dimethyl sulfoxide (DMSO), hexamethyl phosphoramide (HMPA), hexamethyl phosphorous triamide (HMPT), acetonitril, acetone, ethyl acetate, dichloromethane, and tetrahydrofuran (THF). More preferably the strong aprotic solvent is selected from the group consisting of N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl acetamide (DMA), DMSO (dimethyl sulfoxide), hexamethyl phosphoramide (HMPA), and hexamethyl phosphorous triamide (HMPT).

Examples

Example 1

Commercial Torlon® based membranes (obtained from SolSep B.V.) were used for cross-linking. The membranes were first dried at 150°C for 12 h to remove water and then immersed into the cross-linking solution containing 70 wt% (v/v) tetrahydrofuran (THF), 14% (v/v) hexamethylene diisocyanate (HMDI) as cross-linking agent, a mixture of catalysts: 7% (v/v) triethylene diamine (TEA), 5% (v/v) NMP, and 4% (v/v) tin 2-ethylhexanoate as a co-catalyst, for 13 days at 50°C. The reaction was performed in a closed container to ensure water free environment. Then the membranes were removed from the solution and rinsed carefully for 48 h in THF, then 8 h in methanol and finally 8 h in acetone. The resulting membranes were dried at ambient temperature.

The transport properties (flux and retention) of the non-cross-linked and cross-linked membranes were tested in a custom made cross-flow high pressure permeation set up employing acetone and polystyrene (PS) / acetone solutions (Dutczak, Luiten-Olieman et al. 2011, *J. Membr. . Sci*, **372**(1-2): 182-190).

All permeation experiments were performed at 25°C in a total recycle mode at a cross-flow velocity of the feed solution above 2 m/s. Before starting the flux or MWCO measurement, the membrane was always pressurized at the test pressure for minimum 2 h to reach the steady state conditions. The permeance coefficient, P [$l.m^{-2}.h^{-1}.bar^{-1}$], was calculated from the slope of the flux (J, [$l.m^{-2}.h^{-1}$]) vs. transmembrane pressure (TMP) graph. Determination of the acetone permeance was always carried out first. Afterwards, the permeation of 0.3% (w/w) PS mixture was performed in order to obtain MWCO curves. For the cross-linked membranes, besides acetone, the transport of pure NMP was measured as well. After this, the permeation of PS-acetone solution was repeated to compare the flux and MWCO curves with those obtained before NMP transport.

Table 1 shows a performance comparison of non-cross-linked and cross-linked Torlon® based membranes.

Table 1

System	Permeance [$l.m^{-2}.h^{-1}.bar^{-1}$]	
	Non-cross-linked	Cross-linked
Acetone	7.6	1.2
NMP	dissolves	0.1
Acetone-polystyrene (0.3 % w/w)	5.7	1.1

Figure 1 shows an example of the morphology of a non-cross-linked Torlon® based membrane. When this membrane is cross-linked in the absence of NMP, cross-linking is incomplete and the membrane partly dissolves during filtration in NMP (Figure 2)

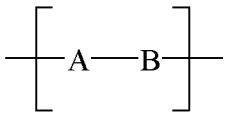
When the membrane is cross-linked in the presence of NMP, no compaction or dissolution of the membrane occurs during filtration in NMP (Figure 3).

Figure 4a shows that the permeance of acetone and PS / acetone mixture through the cross-linked membrane is lower that the non cross-linked membrane. Whereas the non cross-inked membrane dissolves in NMP, the cross-linked membrane stays intact in NMP. After NMP filtration through the cross-linked membrane, the acetone and acetone-polystyrene fluxes are equal to those prior to NMP filtration (Figure 4b).

Figures 5a,b show retention curves of polystyrene (PS) for the non-cross-linked and the cross-linked membrane before and after filtration. The membrane retention increases with cross-linking. The retention of PS also does not change after filtration of NMP (Figure 5b). These two observations show that cross-linking of the polyimide was successful.

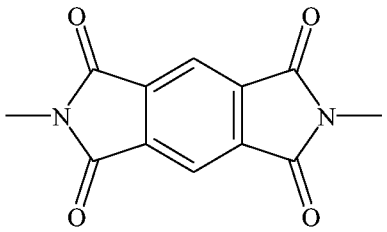
Claims

1. A process for cross-linking a membrane comprising a polyimide, wherein the polyimide is cross-linked with a cross-linking agent comprising two or more isocyanate groups, the polyimide being a polyimide according to Formula (1):

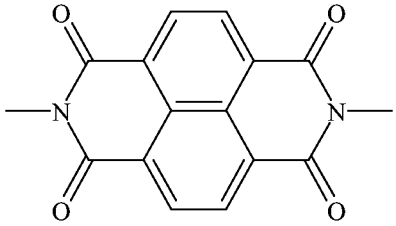


(1)

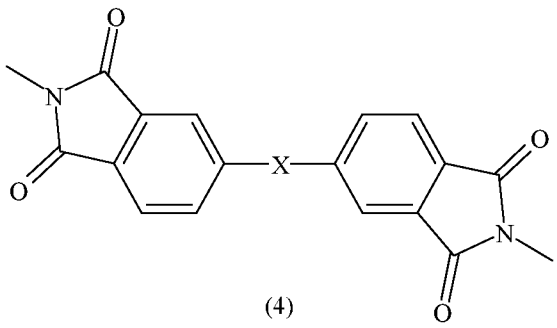
wherein recurring unit A is independently selected from the group consisting of the structures according to Formulas (2) - (4):



(2)



(3)



(4)

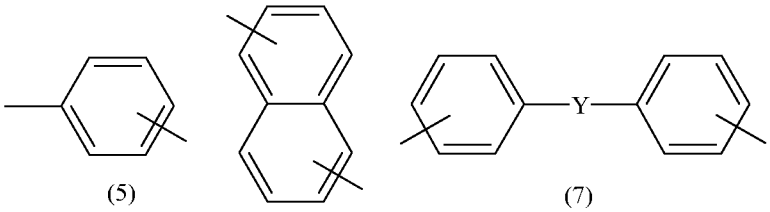
wherein X:

(a) is absent (so that the two aryl groups are connected via a direct bond);

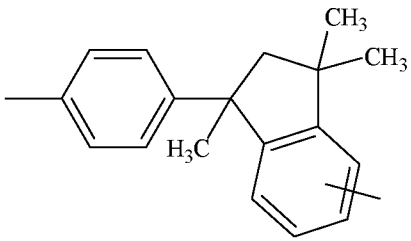
(b) -C(O)-; and

(c) $-(CR^1_2)_n-$, wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5;

wherein recurring unit B is independently selected from the group consisting of the structures according to Formulas (5) - (8):



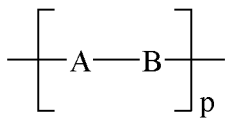
(5) (6) (7)



(8)

wherein Y is independently selected from the group consisting of -C(O)-, -$(CR^1{}_2)_n$-, -O-, -S-; -S(O)-, and -$S(O)_2$-; wherein R^1 is H, F or CF_3 and wherein n = 1, 2, 3, 4 or 5, provided that in Formula (1) recurring unit A has not the structure according to Formula (2) when recurring unit B has the structure according to Formula (7) when Y is O.

2. The process according to Claim 1, wherein the polyimide is a polyimide according to Formula (1a):



(1a)

wherein p is such that the molecular weight of the polyimide is about 10.000 to about 1.000.000 Dalton.

3. The process according to Claim 1 or Claim 2, wherein the cross-linking agent comprises two or three isocyanate groups.

4. The process according to any one of Claims 1 - 3, wherein the cross-linking agent is selected from the group consisting of C_1 - C_{20} alkylene diisocyanates and C_6 - C_{20} arylene diisocyanates.

5. The process according to any one of Claims 1 - 4, wherein the process is performed in a solvent for the polyimide.

6. The process according to Claim 5, wherein the solvent comprises a polar, aprotic solvent.

7. The process according to Claim 6, wherein the polar, aprotic solvent has a dielectric constant ε of at least about 2 at 20°C.

8. The process according to any one of Claims 5 - 7, wherein the polar, aprotic solvent is selected from the group consisting of NMP, DMSO, THF, DMA, DMF, γ-butyrolactone, dioxane, cyclopentanone, and cyclohexanone.

9. The process according to any one of Claims 1 - 8, wherein the process is performed in the presence of a catalyst.

10. A membrane obtainable by the process according to any one of Claims 1 - 9.

11. The membrane according to Claim 10, wherein the membrane has a cut-off point of about 100 to about 10000 Dalton.

12. Use of a membrane according to Claim 10 or Claim 11 in a separation process.

13. Use of a membrane according to Claim 10 or Claim 11 in a membrane separation process comprising a solvent for a non-crosslinked polyimide.

14. Use of a membrane according to Claim 10 or Claim 11 as a support in a pervaporation, nanofiltration or reverse osmosis process, wherein the membrane comprises a selective top layer.

15. A process for separating a dissolved component having a molecular weight of about 100 to about 10000 Dalton from a solution, said process comprising:

(a) contacting the solution with a membrane according to Claim 10 or Claim 11; and

(b) isolating or concentrating the component.

16. The process according to Claim 15, wherein the process is performed under a pressure of about 0.1 kPa to about 5 MPa.

17. The process according to Claim 15 or Claim 16, wherein the process is performed at a temperature of about -10° to about 200°C.

Fig 1

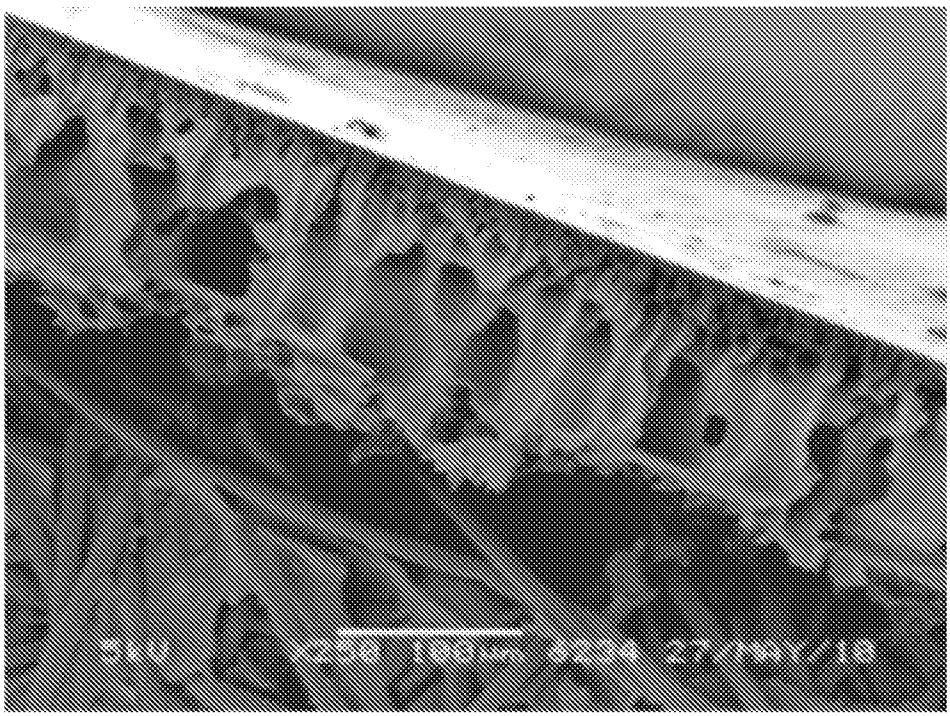


Fig 2

Fig 3

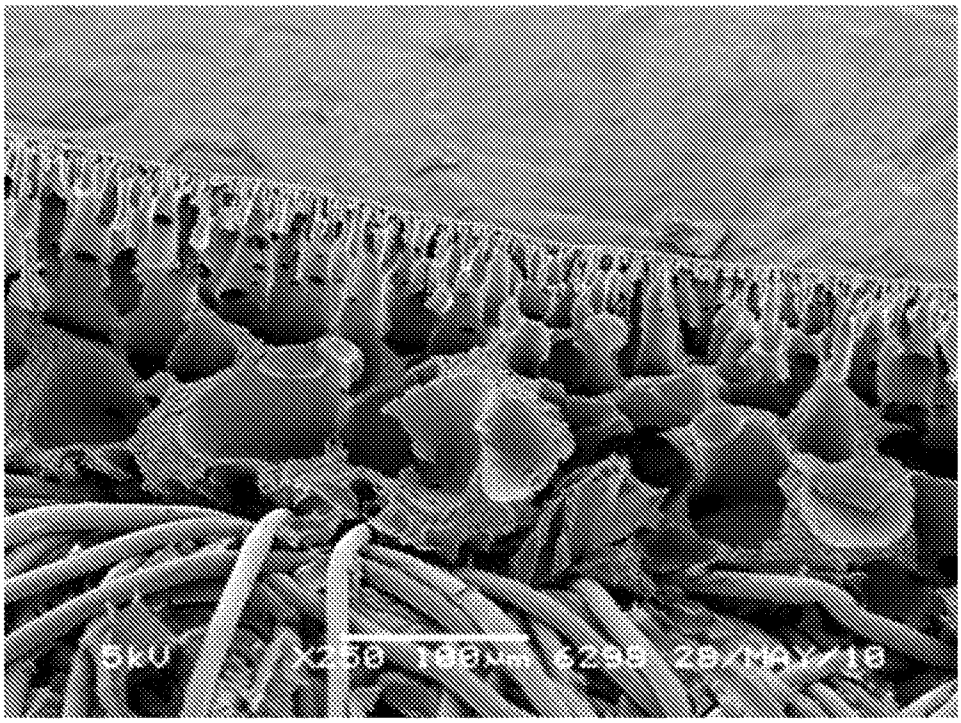


Fig 4a

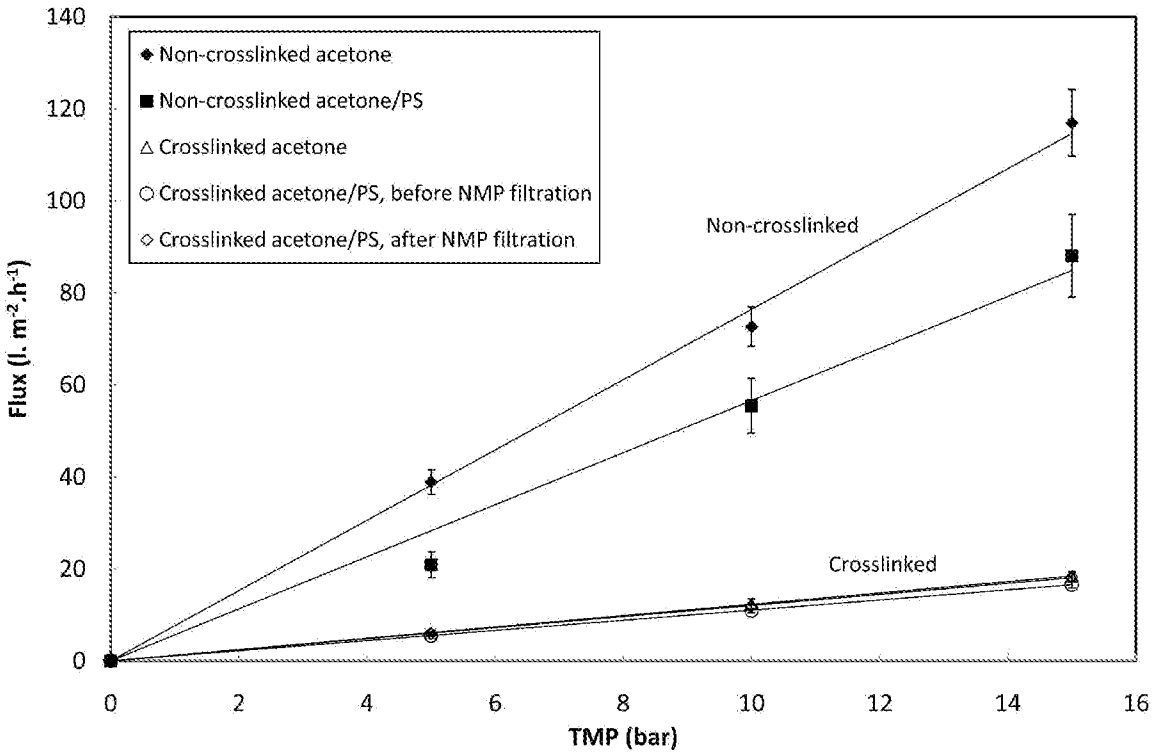

Non-crosslinked acetone
Non-crosslinked acetone/PS
Crosslinked acetone
Crosslinked acetone/PS, before NMP filtration
Crosslinked acetone/PS, after NMP filtration
Non-crosslinked
Crosslinked
Flux (l. m-2.h-1)
TMP (bar)
0
20
40
60
80
100
120
140
0
2
4
6
8
10
12
14
16

Fig 4b

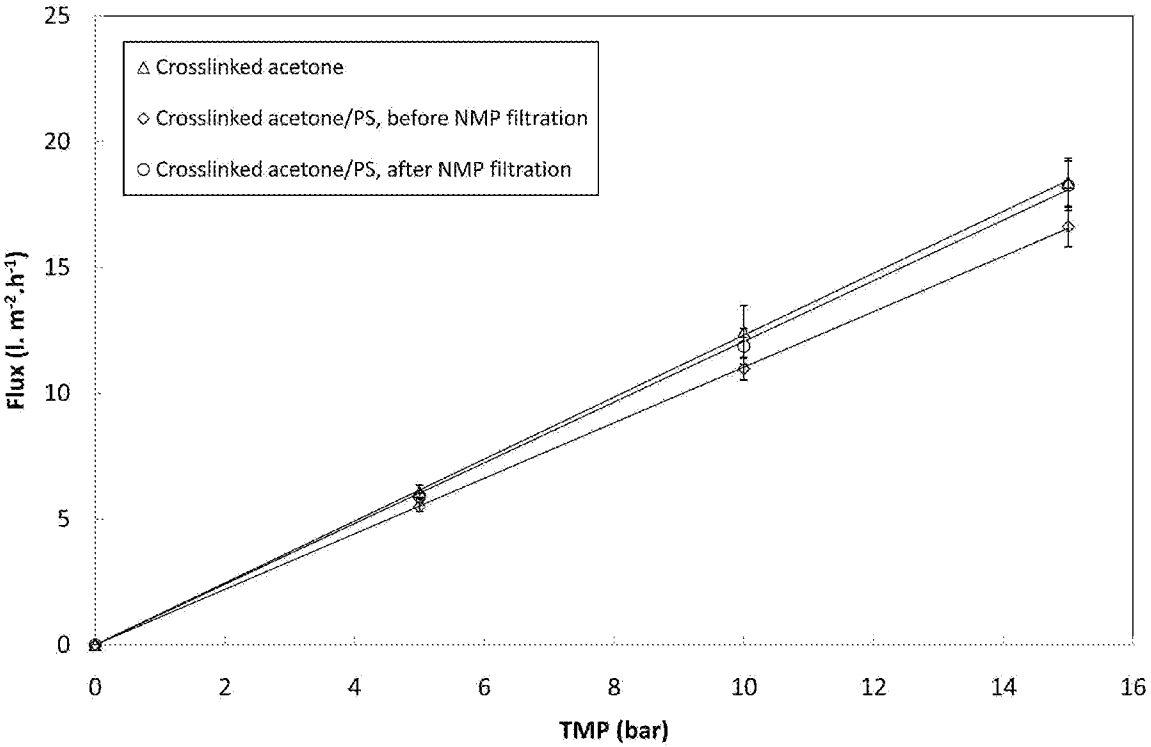

Crosslinked acetone
Crosslinked acetone/PS, before NMP filtration
Crosslinked acetone/PS, after NMP filtration
Flux (l. m-2.h-1)
TMP (bar)
0
5
10
15
20
25
0
2
4
6
8
10
12
14
16

Fig 5a

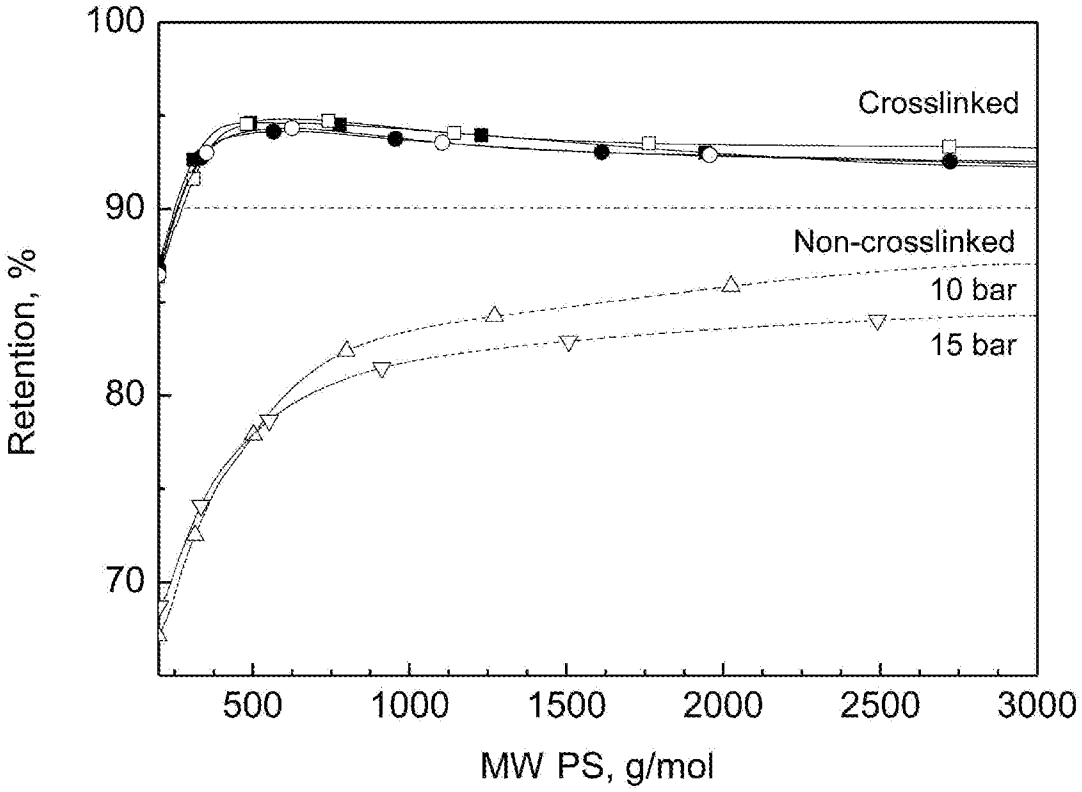
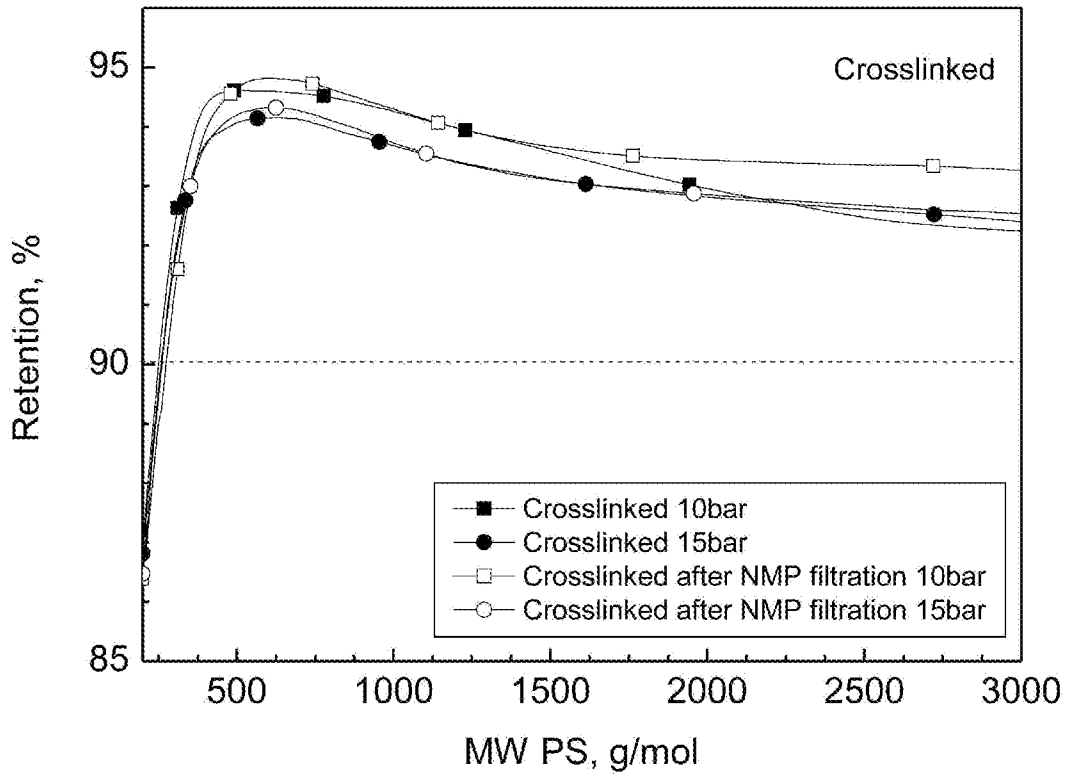

100
90
80
70
Retention, %
Crosslinked
Non-crosslinked
10 bar
15 bar
500
1000
1500
2000
2500
3000
MW PS, g/mol

Fig 5b


95
90
85
Retention, %
Crosslinked
Crosslinked 10bar
Crosslinked 15bar
Crosslinked after NMP filtration 10bar
Crosslinked after NMP filtration 15bar
500
1000
1500
2000
2500
3000
MW PS, g/mol

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2012/050440

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D71/64 B01D67/00 B01D69/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 075 093 A (WALCH AXEL ET AL) 21 February 1978 (1978-02-21)	1-17
Y	column 4, line 67 - column 5, line 33; claim 1; examples 2, 8 the whole document	1-17

	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 August 2012	10/08/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Veríssimo, Sónia

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2012/050440

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DELIGOZ H ET AL: "Preparation, characterization and dielectric properties of 4,4-diphenylmethane diisocyanate (MDI) based cross-linked polyimide films", EUROPEAN POLYMER JOURNAL, PERGAMON PRESS LTD. OXFORD, GB, vol. 42, no. 6, 1 June 2006 (2006-06-01), pages 1370-1377, XP025170439, ISSN: 0014-3057, DOI: 10.1016/J.EURPOLYMJ.2005.12.005 [retrieved on 2006-06-01]	1-17
Y	abstract 1-2.3.3; 3.2; 3.4.2; 3.5; table 2; compound 1 (b) the whole document	1-17

X	BERSHTEIN V A ET AL: "Poly(imide-amide)-poly(ethylene adipate) hybrid networks. I. Nanostructure and segmental dynamics", POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 43, no. 25, 1 January 2002 (2002-01-01), pages 6943-6953, XP004389463, ISSN: 0032-3861, DOI: 10.1016/S0032-3861(02)00665-1	1-17
Y	abstract 2.1; 4; Scheme 1 the whole document	1-17

Y	US 2010/038306 A1 (LIVINGSTON ANDREW GUY [GB] ET AL) 18 February 2010 (2010-02-18) paragraph [0010]; claim 1 the whole document	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2012/050440

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4075093 A	21-02-1978	AT 345761 B	10-10-1978
		BE 834848 A1	16-02-1976
		DE 2450670 A1	29-04-1976
		FR 2288728 A1	21-05-1976
		GB 1494414 A	07-12-1977
		IE 41453 B1	02-01-1980
		IT 1039890 B	10-12-1979
		JP 51082218 A	19-07-1976
		US 4075093 A	21-02-1978
US 2010038306 A1	18-02-2010	CA 2649238 A1	08-11-2007
		CN 101432060 A	13-05-2009
		EP 2012909 A1	14-01-2009
		GB 2437519 A	31-10-2007
		US 2010038306 A1	18-02-2010
		WO 2007125367 A1	08-11-2007