

A Method of Treating a Permeable Membrane

Technical Field

The present invention generally relates to a method of treating a permeable
5 membrane, a treated permeable membrane and to a process for separating fluid mixtures
using the membrane.

Background

The separation of fluid mixtures has been accomplished by various means such as
10 distillation, filtration and solvent extraction. For separation of liquid mixtures, distillation
methods are expensive as they require high amounts of energy to affect a phase change in
the liquid mixture. Furthermore, filtration and solvent extraction may be inadequate in
satisfactorily separating component mixtures.

Membrane separation techniques have been utilized to separate mixtures of two or
15 more different molecules, such as, aqueous mixtures, mixed hydrocarbons, azeotropic
mixtures, and the like.

Some organic solvents, such as low molecular weight alcohols, ketones, ethers and
acids, are completely miscible with water and form azeotropes with water. This makes it
difficult to obtain the anhydrous form of these compounds by conventional separation
20 processes. Compared to conventional processes, i.e. distillation or adsorption,
pervaporation is very promising because of its energy saving aspect and high effectiveness
for azeotropic separation and solvent recovery.

Pervaporation uses a membrane as a barrier to separate liquid mixtures, in which
one side of the membrane is in contact with feed liquid while the other side of the
25 membrane is subjected to vacuum or a carrier gas is applied. Among the polymeric
materials being investigated, polyvinyl alcohol (PVA) membranes are the most popular one
for alcohols or other organics. The most likely reason for this is because PVA is a highly
hydrophilic polymer and has unique film-forming characteristics, controllable
hydrophilicity and good chemical-resistant properties. One known multilayer composite
30 membrane for pervaporation processes has been developed with a crosslinked PVA or
cellulose acetate thin layer on top of polyacrylonitrile, polysulfone. However, most PVA
membranes and other membranes made from highly hydrophilic materials, such as
cellulose acetate and chitosan, are restricted to use in feed waters having a low water
content. This because the PVA membranes tend to swell in aqueous solutions, which
35 dramatically reduces the selectivity of the PVA membrane.

Many attempts have been implemented in order to find appropriate materials for pervaporation dehydration. As a potential candidate, aromatic polyimides possess a number of valuable physico-mechanical and chemical properties. Aromatic polyimides are promising candidates for pervaporation because they exhibit excellent thermal stability as they can be used at temperatures up to 200°C. In addition, some polyimides are stable to organic solvents and concentrated acids (excluding sulfuric and nitric acid).

Asymmetric membranes with an ultra-thin selective layer have been utilized because they have good selectivity and the permeability. However, in practice, it is difficult to obtain membranes with a thin defect-free selective layer.

The dehydration of alcohols using pervaporation processes has received intensive attention because of its potential in industrial applications. Low molecular weight alcohols are miscible with water and form azeotropes which cannot be easily separated by distillation but can be effectively broken up by pervaporation. The feed components may not only dissolve into the membrane and alter the polymer chains conformation but may also subsequently modify separation performance through polymer-penetrant interactions. Therefore, the feed chemistry and physicochemical properties play important roles in the separation performance of a pervaporation membrane.

Most research studies on pervaporation dehydration of alcohols have focused on highly hydrophilic materials, such as poly(vinyl alcohol) (PVA), chitosan and alginate. These kinds of materials usually have solubility parameters close to that of water. Thus, water may act as a predominant plasticizer, swell the membrane chains, and reduce membrane separation performance even if these materials were cross-linked.

Polyimides are promising materials for the pervaporation dehydration of alcohols due to their superior chemical resistance, mechanical properties and lower hydrophilicity, rendering allowing them to be independent of feedwater content. However, despite P84's solvent-resistant character, P84 films can be affected by solvents such as alcohols. For example, one study found that pretreatment of P84 films by immersing the films into different alcohol solutions for one day is capable of adjusting the gas-separation performance of the derived polyimide membranes. It is thought that this may be due to swelling problems swelling induced by the affinity between alcohol and P84 membranes. Alcohols such as ethanol, IPA, and tert-butyl alcohol are important protic solvents with high polarity and can form strong interactions with polymers containing imide groups through polar-polar interaction, hydrogen bonding, or other interactions. These interactions can alter the polymer chain packing density or chain mobility.

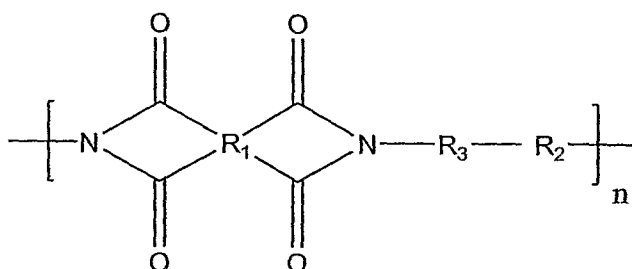
There is a need to provide a method of treating a permeable membrane, a permeable membrane and a process for separating fluid mixtures using the treated membrane, that overcomes or at least ameliorates one or more of the disadvantages described above.

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Summary

According to a first aspect, there is provided a method of treating a permeable membrane comprising the steps of:

- (a) providing a permeable membrane comprising a copolymer having (n) repeating units of general formula (I):



(I)

wherein R_1 and R_2 are aromatic hydrocarbon moieties, and

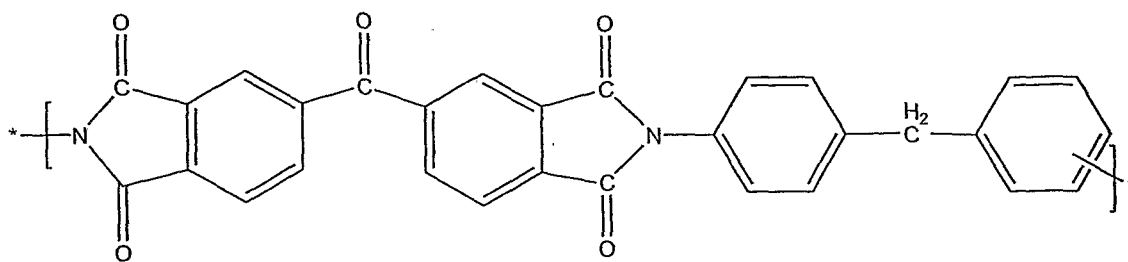
- R_3 is an optional moiety and is selected from the group consisting of alkyls and aromatic hydrocarbons;

- (b) heating said permeable membrane for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating; and
(c) forming a permeable sealant layer on at least one side of said membrane.

Advantageously, the permeable sealant layer covers any voids present in said membrane to at least partially enhance the selectivity of the membrane.

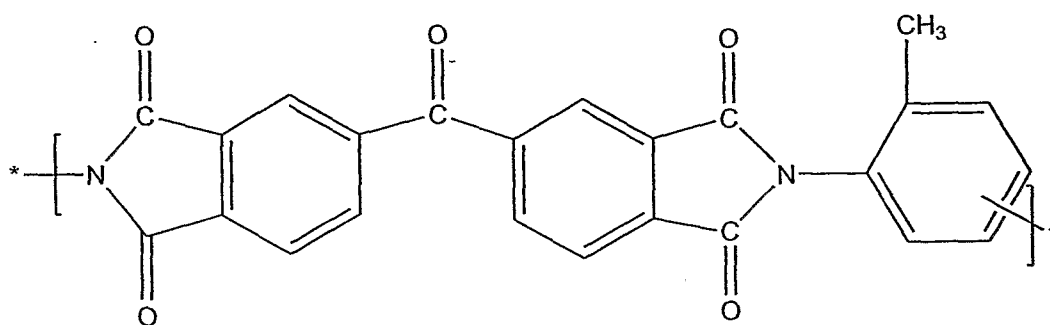
In one embodiment, there is provided a method of treating a permeable membrane comprising the steps of:

- (a) providing a permeable membrane comprising a copolyimide polymer having (n) repeating units, wherein between 10% to 90% of said imide linkages having the following structural formula (IV):



(IV)

and wherein the remainder have imide linkages having the following structural formula (V):



(V)

5 ; and

(b) heating said permeable membrane for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating; and

(c) forming a permeable sealant layer on at least one side of said membrane.

According to a second aspect, there is provided a membrane separation process for
10 separating mixtures of fluids having at least a two fluid components that permeate through a membrane at different rates, the process comprising the steps of:

(a) providing a two-sided treated selectively permeable membrane made in the method of the first aspect, as defined above;

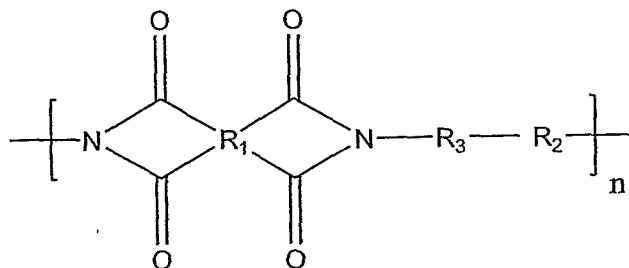
15 (b) contacting a first side of the membrane with a feed mixture comprising said mixtures of fluids; and

(c) causing the feed mixture to selectively permeate through the membrane and thereby form, on the second side of the membrane, a permeate composition which has a concentration of one of the fluid components that is greater than that of the feed mixture.

20 According to a third aspect, there is provided a membrane separation process for separating a mixture of an aqueous liquid and an organic liquid comprising compounds

having at least three carbon atoms, the membrane separation process comprising the steps of:

(a) providing a permeable membrane comprising a copolymer having (n) repeating units of general formula (I):



(I)

wherein R₁ and R₂ are aromatic hydrocarbon moieties,

R₃ is an optional moiety and is selected from the group consisting of alkyls and aromatic hydrocarbons, and

wherein said permeable membrane has undergone heat treatment for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating;

(b) providing, on a first side of the membrane, a feed mixture comprising said mixtures of aqueous liquid and organic liquid; and

(c) causing said feed mixture to selectively permeate through the membrane and thereby form, on the second side of the membrane, a permeate composition which has a lower organic liquid concentration than that of the feed mixture. Optionally in said third aspect, said permeable membrane comprises a permeable sealant layer on at least one side of said membrane.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term "moiety", and grammatical variations thereof, is used to refer to a specific segment or part of a molecule.

The term "aromatic hydrocarbon moiety", and grammatical variations thereof, is used herein to designate a hydrocarbon-based organic moiety containing one or more aromatic rings, e.g. fused and/or bridged, having at least one hydrogen atom removed. An aromatic ring is typified by benzene having a single aromatic nucleus with at least one hydrogen removed from the ring. Aromatic hydrocarbon moieties having more than one

aromatic ring include, for example, radicals of naphthalene, anthracene, etc. Exemplary aromatic hydrocarbons useful in the disclosed embodiments include those having 1 to 2 aromatic rings.

5 The term "alkyl" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 10 carbon atoms, eg, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like.

15 The term "ether" and grammatical variations thereof includes moieties which contain an oxygen bonded to two different carbon atoms.

The term "epoxide" and grammatical variations thereof is to be understood to mean a moiety that contains an oxirane three member ring containing an oxygen that is bonded to two carbon atoms in a chain.

20 The term "ester" includes moieties which contain a carbon bound to an oxygen atom which is bonded to the carbon of a carbonyl group.

The term "sulfonyl", as used herein, means a -SO₂ group.

The term "carbonyl", as used herein, means a -C=O group or a -CHO group.

25 The term "organic liquid" is used to describe compounds mainly comprising at least three carbon atoms, hydrogen atoms, and, in some cases, containing oxygen atoms, sulfur atoms or nitrogen atoms. Exemplary classes of organic liquids which can be used include alcohols, ketones, aromatic hydrocarbons, aliphatic unsaturated hydrocarbons, ethers, esters, cycloaliphatic hydrocarbons, and mixtures thereof.

30 Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

35 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the

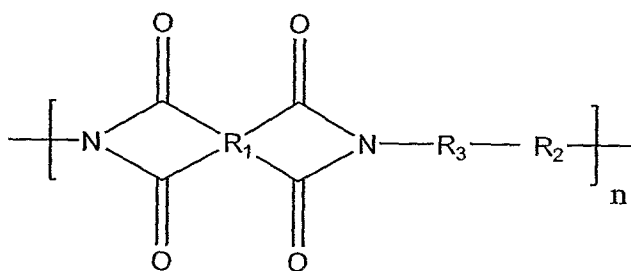
scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a method of treating a permeable membrane, will now be disclosed. The method comprises the steps of:

A method of treating a permeable membrane comprising the steps of:

(a) providing a permeable membrane comprising a copolymer having (n) repeating units of general formula (I):



(I)

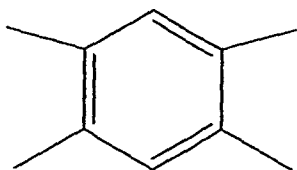
wherein R_1 and R_2 are aromatic hydrocarbon moieties, and

R_3 is an optional moiety and is selected from the group consisting of alkyls and aromatic hydrocarbons;

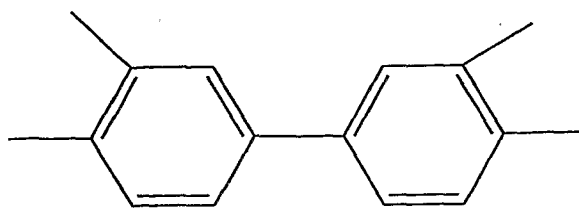
(b) heating said permeable membrane for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating; and

(c) forming a permeable sealant layer on at least one side of said membrane.

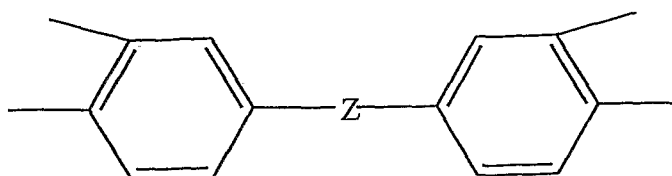
In one embodiment, the R_1 moiety is of composition selected from the group consisting of formula (A), formula (B), formula (C) and mixtures thereof,



(A)



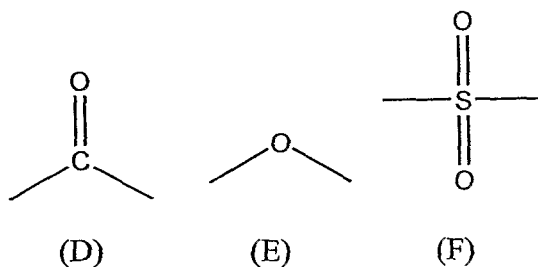
(B)



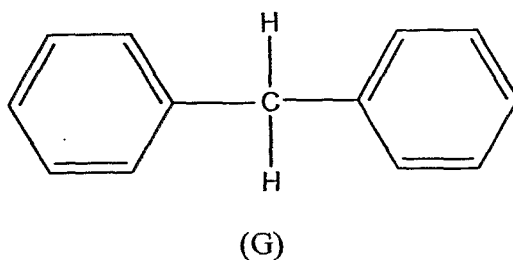
(C)

wherein Z is a moiety selected from the group consisting of ethers, epoxides, esters,
5 carbonyls sulfonyls and mixtures thereof.

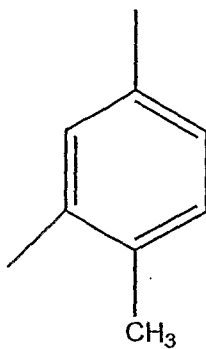
In one embodiment, Z has a composition selected from the group consisting of
formula (D), formula (E), formula (F) and mixtures thereof,



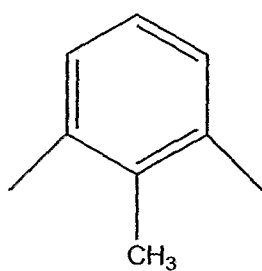
In one embodiment, the R₂ is a moiety of composition selected from the group
10 consisting of formula (G), formula (H), formula (I) and mixtures thereof,



(G)

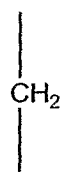


(H)

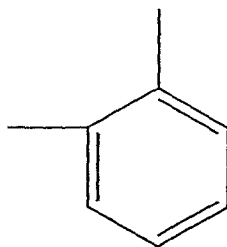


(I)

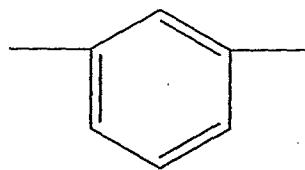
In one embodiment, the R_3 is a moiety of composition selected from the group consisting of formula (J), formula (K), formula (L), formula (M), formula (N), formula (O) and mixtures thereof,



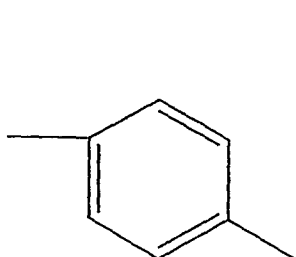
(J)



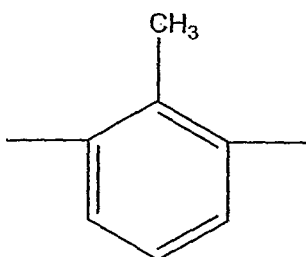
(K)



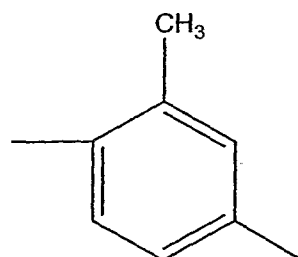
(L)



(M)

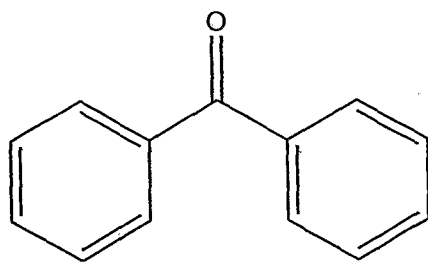


(N)



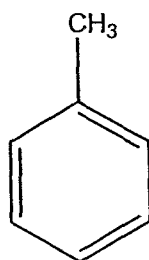
(O)

In one embodiment, R_1 has the composition of formula (P)



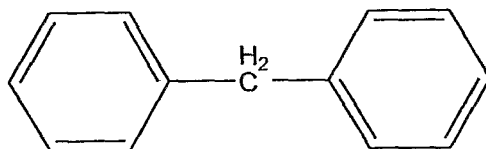
(P)

In one embodiment, R₃ has the composition of formula (Q)



(Q)

In one embodiment, R₂ has the composition of formula (R)

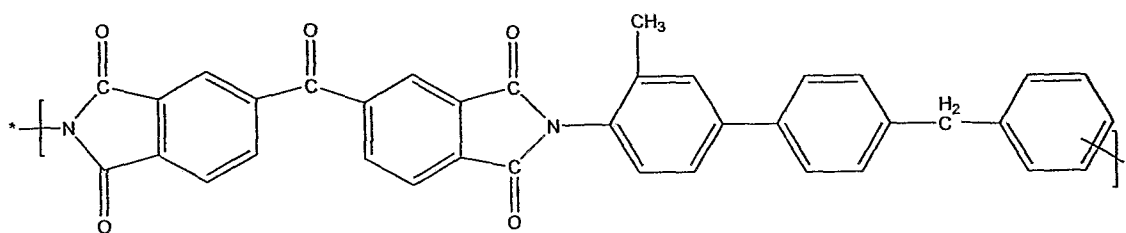


(R)

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In one embodiment, the providing step (a) comprises the step of:

(a1) providing the permeable membrane comprising a copolymer having (n) repeating units of formula (VI):



(VI)

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In one embodiment, the forming step (c) comprises the step of:

(c1) forming a water-permeable layer on said at least one side of said membrane.

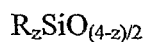
The water permeable layer may be selected from the group consisting of polysiloxanes, such as, for example, polydimethylsiloxanes or polysiloxanes comprising

alkyl and aryl substituents on the silicon atom, copolymers of dimethylsiloxane and phenylenesilane; copolymers of dimethylsiloxane and polyurethane; organopolysiloxane/polycarbonate copolymers; polyvinylpyridines and copolymers thereof.

5 In one embodiment, the forming step (c1) comprises the step of:

(c2) forming a water-permeable silicone elastomer layer on said at least one side of said membrane. The silicone elastomer may comprise an organopolysiloxane, such as a dialkylsiloxane polymer. The organopolysiloxane may be selected from the group of organopolysiloxanes having the following average compositional formula:

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wherein the letter z is a positive number from 1.98 to 2.02

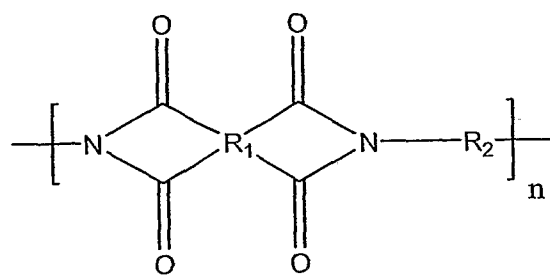
15 R_z may be the same or different, and is a substituted or unsubstituted monovalent hydrocarbon groups of 1 to 12 carbon atoms or 1 to 6 carbon atoms, for example, alkyl groups such as methyl, ethyl, propyl and butyl; cycloalkyl groups such as cyclohexyl; alkenyl groups such as vinyl, allyl, butenyl and hexenyl; aryl groups such as phenyl and tolyl; aralkyl groups such as benzyl and β-phenylpropyl; and substituted ones of the foregoing groups in which some or all of the hydrogen atoms attached to carbon atoms are
20 replaced by halogen atoms, cyano groups or the like, such as chloromethyl, trifluoropropyl and cyanoethyl. The organopolysiloxane may have at least two alkenyl groups per molecule. The organopolysiloxane may be end-capped with trimethylsilyl, dimethylvinylsilyl, dimethylhydroxysilyl or trivinylsilyl groups.

25 Exemplary organopolysiloxane may include dimethylpolysiloxane, methylphenylpolysiloxane, copolymer of dimethylsiloxane and methylphenylsiloxane, methylvinylpolysiloxane, and copolymer of dimethyl siloxane and methylvinylsiloxane of which the terminal ends are blocked by silanol groups.

In one embodiment, the forming step (c) comprises the step of:

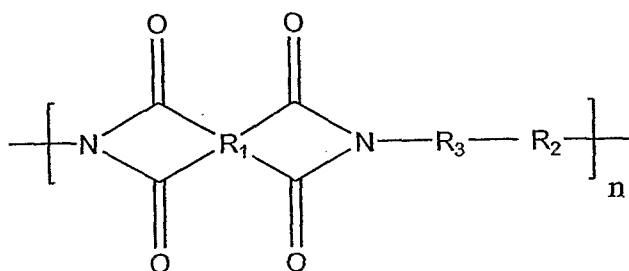
30 (c1) forming a polysiloxane layer on at least one side of said membrane. The polysiloxane layer may be poly-dimethylsiloxane.

In one embodiment, the copolymer has between 10% to 90% imide linkages having the following structural formula (II):



(II)

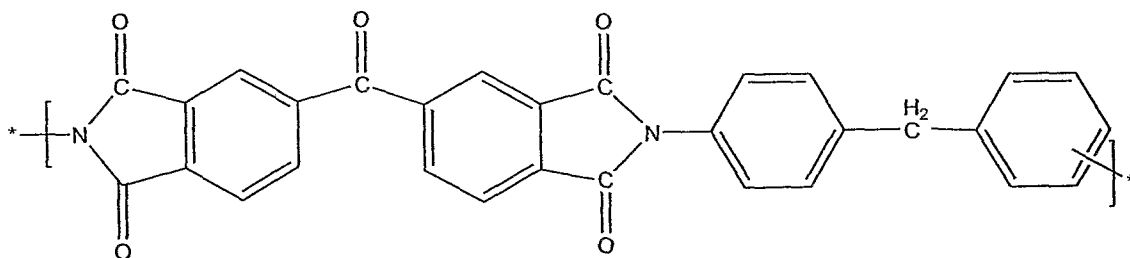
and wherein the remainder have imide linkages having the following structural formula (I):



(I)

wherein R₃ is not optional.

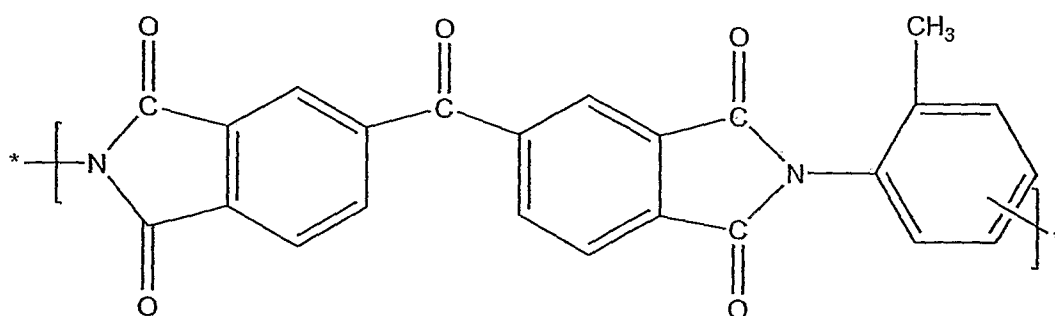
5 In one embodiment, the copolymer has between 10% to 90%, or 70 to 90%, imide linkages having the following structural formula (IV):



(IV)

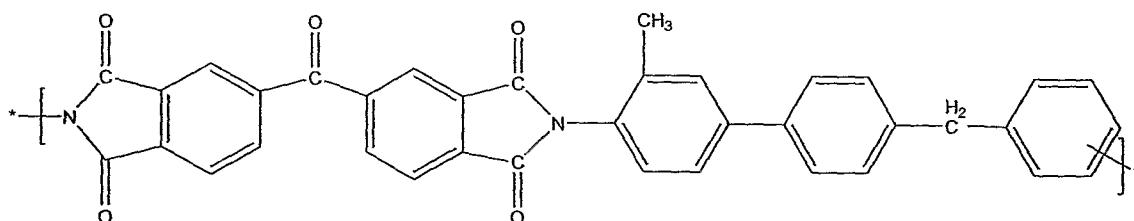
and wherein the remainder have imide linkages having the following structural formula

10 (V):



(V)

In one embodiment, the copolymer has between imide linkages having the following structural formula (VI):



(VI)

The heating step (b) may comprise the step of:

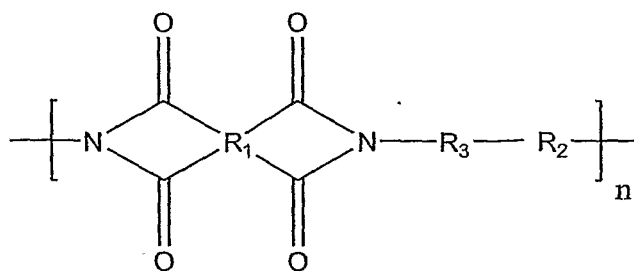
(b1) heating said permeable membrane at a temperature in the range selected from the group consisting of: 60°C to 400°C, 100°C to 400°C, 150°C to 400°C, 200°C to 400°C, 250°C to 400°C, 300°C to 400°C, 200°C to 300°C and 200°C to 350°C.

The heating step (b) may comprise the step of:

(b1) heating said permeable membrane for a time selected from the group consisting of 1 minute to 1500 minutes, 100 minutes to 1500 minutes, 250 minutes to 1500 minutes, 350 minutes to 1500 minutes, 500 minutes to 1500 minutes, 1000 minutes to 1500 minutes.

In one embodiment, there is provided a membrane separation process for separating a mixture of an aqueous liquid and an organic liquid comprising compounds having at least three carbon atoms, the membrane separation process comprising the steps of:

(a) providing a permeable membrane comprising a copolymer having (n) repeating units of general formula (I):



(I)

wherein R_1 and R_2 are aromatic hydrocarbon moieties,

R_3 is an optional moiety and is selected from the group consisting of alkyls and aromatic hydrocarbons, and

5 wherein said permeable membrane has undergone heat treatment for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating;

(b) contacting a first side of the membrane with a feed mixture comprising said mixtures of aqueous liquid and organic liquid; and

10 (c) causing the feed mixture to selectively permeate through the membrane and thereby form, on the second side of the membrane, a permeate composition which has a lower organic liquid concentration than that of the feed mixture.

In one embodiment, the membrane separation process further comprises the step of:

15 (d) heating said feed mixture to cause one of said aqueous liquid to form a vapor and permeate through said membrane.

In one embodiment, the membrane separation process further comprises the step of:

(e) removing, from the second side of the membrane, said vapor that has permeated through said membrane.

The aqueous liquid may be water. The organic liquid may include organic
20 compounds having at least 3 carbon atoms. In one embodiment, the organic liquid comprises organic compounds having 3 carbon atoms, 3 to 12 carbon atoms, or 4 to 12 carbon atoms, or 5 to 12 carbon atoms, or 6 to 12 carbon atoms, or 3 to 4 carbon atoms or 3 to 5 carbon atoms, or 3 to 6 carbon atoms, or 3 to 7 carbon atoms, or 3 to 8 carbon atoms. Exemplary organic liquids include alcohols, ketones, aromatic hydrocarbons, aliphatic
25 unsaturated hydrocarbons, ethers, esters, cycloaliphatic hydrocarbons, and mixtures thereof.

The organic liquid may be an alcohol selected from the group consisting of saturated aliphatic alcohols having a carbon atom of between 3 to 8, unsaturated aliphatic alcohols having a carbon atom of between 3 to 8, alicyclic alcohols having a carbon atom

of between 3 to 8, aromatic alcohols having a carbon atom of between 3 to 8, heterocyclic alcohols having a carbon atom of between 3 to 8 and mixtures thereof. Exemplary alcohols which can be used as organic liquids include saturated aliphatic alcohols such as propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, amyl alcohol, isoamyl alcohol, hexyl alcohol, etc.; unsaturated aliphatic alcohols such as allyl alcohol, crotyl alcohol, propargyl alcohol, etc.; alicyclic alcohols such as cyclopentanol, cyclohexanol, etc.; aromatic alcohols such as benzyl alcohol, cinnamyl alcohol, etc.; heterocyclic alcohols such as furfuryl alcohol, etc.; and mixtures thereof.

Exemplary ketones which can be used as organic liquids include saturated aliphatic ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl butyl ketone, methyl isobutyl ketone, butyrone, diisopropyl ketone, etc.; unsaturated aliphatic ketones such as methyl vinyl ketone, mesityl oxide, methyl heptenone, etc.; alicyclic ketones such as cyclobutanone, cyclopentanone, cyclohexanone, etc.; aromatic ketones such as acetophenone, propiophenone, butyrophenone, etc.; mixtures thereof.

Exemplary esters which can be used as organic liquids are carboxylic acid esters having at least three carbon atoms. Preferred carboxylic acids in the carboxylic acid esters are organic carboxylic acids having 1 to 12 carbon atoms as long as the reactant is an alcohol having 2 to 12 carbon atoms to form a condensation ester product having at least 3 carbon atoms. Examples include saturated aliphatic carboxylic acids, unsaturated aliphatic carboxylic acids, aromatic carboxylic acids, etc. Examples of alcohols in the esters are preferably alcohols having 1 to 10 carbon atoms as long as the reactant is a carboxylic acid to form a condensation ester product having at least 3 carbon atoms.

Exemplary ethers which can be used as organic liquids are saturated aliphatic ethers such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, methyl isopropyl ether, methyl butyl ether, methyl isobutyl ether, methyl n-amyl ether, methyl isoamyl ether, ethyl propyl ether, ethyl isopropyl ether, ethyl butyl ether, ethyl isoamyl ether, etc.; unsaturated aliphatic ethers such as diallyl ether, methyl allyl ether, ethyl allyl ether, etc.; aromatic ethers such as anisole, phenetole, diphenyl ether, etc.; cyclic ethers such as trimethylene oxide, tetrahydrofuran, tetrahydropyran, dioxane, and mixtures thereof.

Exemplary unsaturated aliphatic hydrocarbons which can be used as organic liquids are straight chain, branched chain and cyclic unsaturated aliphatic hydrocarbons such as cyclohexene, dodecene, cycloheptene, cyclopentadiene, cyclopentene, cycloheptadiene, cyclooctatetraene, cyclohexadiene, decene, tetradecene, etc.

Examples of aromatic hydrocarbons which can be used as organic liquids are benzene, toluene, xylene, indene, tetralin, etc.

The weight percentage of organic liquid in said mixture may be in the range selected from the group consisting of: 5% to 95%, 10% to 95%, 15% to 95%, 20% to 95%, 25% to 95%, 30% to 95%, 35% to 95%, 40% to 95%, 45% to 95%, 50% to 95%, 5% to 90%, 5% to 85%, and 5% to 80%.

Advantageously, said heating step (b) is undertaken at a temperature and for a time to increase the selectivity of the membrane for a mixture of isopropanol (IPA) and water, wherein said selectivity factor is at least seven times the selectivity factor of an ethanol and water mixture (EtOH/H₂O) and a methanol/water mixture (MeOH/H₂O).

Advantageously, said heating step (b) and said forming step (c) enhance the flux of said membrane. The membrane may be characterized in that, when said mixture is at 60°C, said membrane flux may be at least 500 gm⁻²hr⁻¹, or at least 600 gm⁻²hr⁻¹, or at least 700 gm⁻²hr⁻¹, or at least 800 gm⁻²hr⁻¹.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Figure 1 shows one-month and three-month sorption results of dense P84™ membranes at room temperature;

Figure 2 shows pervaporation performance at various feed aqueous alcohol mixtures and different temperatures (continuous line, separation factor; dotted line, selectivity);

Figure 3 shows water and alcohol permeances at various feed aqueous alcohol mixtures and different temperatures; and

Figure 4 shows comparison of XRD spectra of dense P84™ membranes after immersion in (a) 85 wt % ethanol/water; (b) 85 wt % IPA/water; (c) 85 wt % tert-butyl alcohol/water; and (d) original dense film.

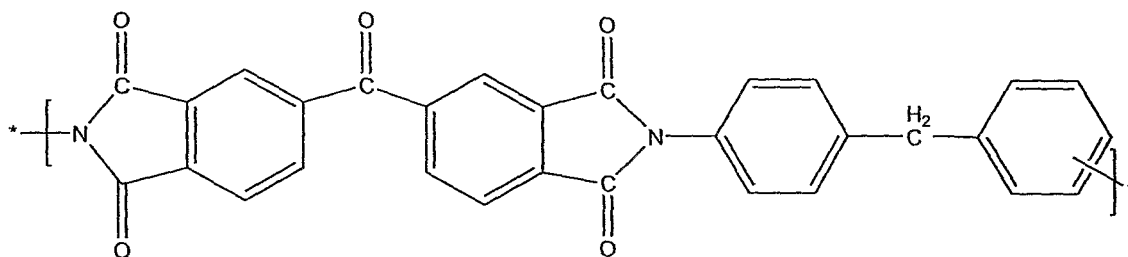
Preparation of membranes

Non-limiting examples of a method for preparing the membranes will be further described.

Polymer

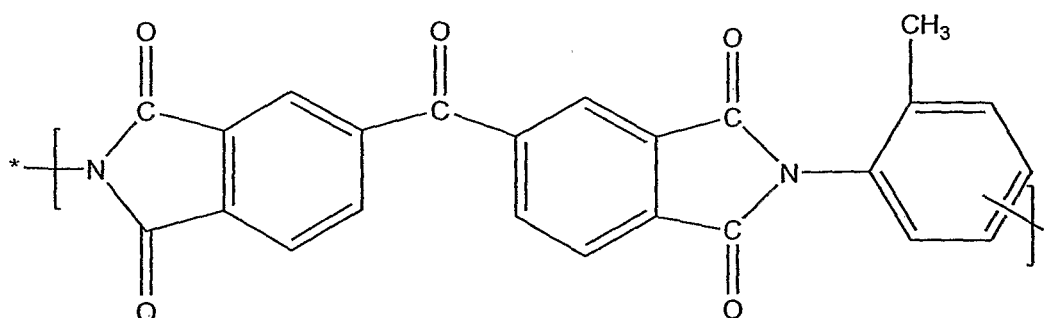
Suitable copolymers for use in the disclosed methods aromatic polyimide polymers, fully imidized, and highly polar copolymer. The polyimide polymers described in U.S. Pat. No. 3,708,458 assigned to Upjohn and which is incorporated in its entirety for reference, may be suitable polyimide polymers used in the disclosed method. The polymer is a copolymer derived from the co-condensation of benzophenone 3,3',4,4'-tetracarboxylic acid dianhydride (BTDA) and a mixture of di(4-aminophenyl)methane and toluene diamine or the corresponding diisocyanates, 4,4'-methylenebis(phenyl isocyanate) and toluene diisocyanate.

The suitable copolyimide has imide linkages which may be represented by the structural formulae (IV) and (V), wherein about 20 % imide linkages have the structural formula (IV):



(IV)

and wherein about 80% have structural formula (V):



(V)

The suitable copolyimide is available commercially as P84™ available from P84™ available from HP Polymer GmbH of Lenzing, Austria. It will however be appreciated

that polymers having similar structures will also be suitable polymers in the disclosed method.

The P84™ co-polyimide was dried overnight at 120°C under vacuum before use.

Preparation of Dense and Asymmetric Flat Membranes

5 Both dense and asymmetric flat membranes were prepared. The P84™ co-polyimide is fully dissolved in selected solvent, with or without non-solvent mixtures, before being degassed overnight prior to membrane fabrication.

10 The dope formula is important for the skin formation. P84™ cannot be dissolved in tetrahydrofuran (THF), chloroform, dichloromethane at room temperature and therefore, it is not preferable to simply choose low boiling point solvents to produce a defect-free membranes. It is preferable for a high boiling point solvent to be employed, with or without the addition of a volatile non-solvent such as acetone, to improve the evaporation and facilitate the skin formation.

15 The volatile non-solvent can also affect the porosity and structure of the membrane. The suitable polymer concentration may be between 15 to 40 wt%, but 18 to 30wt% is preferred.

20 For a flat sheet membrane: the solution was cast onto a glass plate or other support substrate with a casting knife. The particularly suitable membrane thickness is about 20~300µm. The nascent films are blown with air (25 -150 °C) and free evaporate for a certain period (0.001 sec to 10 min) before immersing the film into a coagulation bath. The coagulating medium may consist of water.

To stabilize the membrane and to achieve a better separation performance, the asymmetric membranes were heat-treated with a rate of 0.6 °C/min to 250 °C under vacuum and held there for 6 h prior to use.

25 For hollow fibre fabrication: both polymer solution and bore fluid may be extruded through a spinneret into a coagulation bath to produce hollow fiber membranes. The temperature of coagulation bath and spinneret can be varied from 5 to 80 °C and from 15 to 90 °C, respectively.

30 The asymmetric flat sheet or hollow fiber polyimide membranes can be solvent exchanged in water and dried in air or solvent exchanged with low surface tension liquids e.g. methanol and followed by 10wt% SYLGARD™ 184 in hexane solution, and dried naturally in the air.

The formed membranes normally still have defects and exhibit high flux but relatively low selectivity. Advantageously, the formed membranes are subjected to heat treatment to effectively improve the membrane selectivity as defined above.

The formed membrane may also have defects in its structure, such as voids, which leads to reduced selectivity. To overcome this problem, a permeable sealant is applied to one side of the formed membrane. Exemplary sealants are silicone elastomers, such as poly-dimethylsiloxane, available commercially under the trade name SYLGARD™ 184 from Dow Corning Corporation of the United States of America. The SYLGARD™ 184 is diluted in an organic solvent such as hexane solution. The concentration of SYLGARD™ 184 in hexane solution can be 0.1~10wt%.

It should be realized that the additional permeable sealant layer may be applied to the membrane before or after heat treatment.

Example 1

Pervaporation Experiments and Data Analysis

P84™ co-polyimide membranes were fabricated according to the methods disclosed in *Qiao*[1] and were heat-treated at a rate of 0.6 °C/min to 250 °C under vacuum for 6 hours. A layer of poly-dimethylsiloxane was then applied to the heat treated P84™ co-polyimide membranes.

Pervaporation tests were conducted using a lab-scale Sulzer pervaporation unit [3] and the detailed experimental procedures were reported elsewhere.[1],[2].

An 85/15 (in weight ratio) alcohol/water mixtures were used as the feed. Flux and separation factors were calculated by the following equations

$$J = \frac{Q}{At} \quad (1)$$

$$\alpha_{2/1} = \frac{y_2 / y_1}{x_2 / x_1} \quad (2)$$

where J is the flux, Q is the total mass transferred over time t, A is the membrane area, x_2 and y_2 are the mole fractions of water in the feed and permeate, respectively, and x_1 and y_1 are the mole fractions of alcohol in the feed and permeate, respectively.

On the basis of the solution-diffusion mechanism, the basic transport equation for pervaporation can be written as follows

$$J_i = \frac{P_i}{l} (x_i \gamma_i p_i^s - y_i p^p) \quad (3)$$

where P_i is the membrane permeability, which is the product of the solubility and the diffusivity. Superscripts “s” and “p” correspond to the saturated state and permeate, respectively. “l” is the membrane dense layer thickness. p_i denotes the partial vapor pressure, while P_i/l is the permeance. γ is the activity coefficient. The permeance and selectivity (the permeance ratio) can be calculated from the flux and separation factor following the approach described elsewhere. [1],[3],[4],[5]

Sorption Tests. Dense P84™ membrane strips

(40-90 μm) were dried under vacuum overnight. Then these preweighed dry membrane strips were immersed in pure DI water, ethanol, IPA, and tert-butyl alcohol solutions or 85 wt % alcohol in water solutions, respectively.

The surfaces of swollen samples were blotted between tissue papers then weighed in a closed container at different time intervals. The degree of swelling was calculated from the difference between the wet weight M_{wet} after equilibrium sorption and the dry weight M_{dry} , as follows:

$$\frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \quad (4)$$

For the sorption experiments in 85 wt % alcohol solutions, the sorbed liquid in the membrane was removed by vacuum with aid of heating by boiling water and then collected by cold traps immersed in liquid nitrogen. The sorption selectivity was determined as follows,

$$\alpha_{\text{water / alcohol}}^{\text{sorption}} = \frac{C_2 / C_1}{x_2 / x_1} \quad (5)$$

where C indicates the weight fraction of a sorbed component in the membrane.

Membrane Characterizations

Wide-angle Xray diffraction (XRD) measurements of the membranes were carried out by a Shimadzu XRD-6000 X-ray diffractometer using the Cu K α radiation wavelength ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 30 mA. The average intersegmental distance of polymer chains was reflected by the broad peak center on each X-ray pattern. The d-space was calculated by the Bragg's equation:

$$n\lambda = 2d \sin \Theta \quad (6)$$

where Θ is the X-ray diffraction angle of the peak.

A Mettler-Toledo 822e differential scanning calorimeter (DSC) was used to measure the glass transition point (T_g) of the membrane samples. The temperature range scanned was from 50 to 400 °C at a heating rate of 10 °C/min.

Results and Discussion

Swelling and Sorption of P84™ Dense Membranes.

The sorption tests reflect the affinity between membrane materials and the permeating molecules.

Figure 1 shows the sorption data of P84™ dense films in pure water, ethanol, IPA, and tert-butyl alcohol after 1 month and 3 months. After a 1-month immersion in different media, the membrane immersed in water had the highest degree of swelling. After a 3-month immersion, the membrane immersed in ethanol exhibited the highest degree of swelling. For the membranes immersed in the same medium for different immersion times, the degrees of swelling after the 3-month immersion was higher than those for the 1-month immersion.

Among the different media, ethanol had the highest increase in the degree of swelling with a prolonged immersion time. This indicates that it takes a long time for P84™ membranes to reach the sorption equilibrium because of the rigid and tight glassy polymer chains.

In a short-term sorption, water molecules diffuse faster than alcohol molecules; therefore, the sorption of water in the membrane reached its equilibrium much faster than that of alcohols. Long-term sorption indicates P84™ may have a stronger affinity to ethanol than to water. This phenomenon is in agreement with the solubility parameters listed in Table 1 below, which shows that P84™ and ethanol have the closest solubility parameter.

Table 1. Solubility parameters of P84™, Water, Ethanol, IPA, and *tert*-Butyl Alcohol

Properties	P84™	water	ethanol	IPA	<i>tert</i> -Butyl Alcohol
solubility parameter (MPa) ^{1/2}	26.8 ¹⁹	47.9 ²⁰	26.0 ²⁰	23.5 ²⁰	21.7 ²⁰
Δsolubility parameter* (MPa) ^{1/2}		21.1	0.7	3.4	5.1

Polarity parameter (kcal/mol)	$E_T(30)^{21}$	63.1	51.9	48.4	43.3
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* Δ solubility parameter is the absolute value of (solubility parameter of membrane) – (solubility parameter of solvent)

In addition, ethanol possesses the highest polarity parameter (Table 1) and the strongest hydrogen-bonding ability (proportional to the polarity parameter[6]) among these three alcohols, which implies that the high interactions between polyimide and ethanol are through polar-polar groups and hydrogen bonds.

Table 2 summarizes the 1-month sorption data of dense P84™ films in different aqueous alcohol solutions containing 85 wt % of alcohol. Because of the combination of water and alcohol effects, the sorption of dense P84™ films was 2-3 times greater than that when immersed in pure alcohols. The sorption selectivity shows that water is preferentially absorbed in P84™ membranes, while extremely high sorption selectivity is observed for the aqueous tert-butyl alcohol system.

Table 2. Sorption Results of Dense P84™ membranes in 85 wt % Aqueous Alcohol solutions

Alcohols	Degree of swelling (g/(g of dry membrane))	Sorption selectivity (water/alcohol)
Ethanol	0.037	56
IPA	0.024	660
Tert-butyl alcohol	0.029	4146

The large solubility parameter difference between P84™ and tert-butyl alcohol and the steric hindrance induced by tert-butyl alcohol's large molecular size make P84™ potentially suitable for the pervaporation dehydration of aqueous tert-butyl alcohol mixtures.

Separation Performances of P84™ Asymmetric Membranes in Various Alcohol/Water Mixtures

The pervaporation results for feed alcohol mixtures containing 85 wt % alcohols are shown in Figure 2. The separation factor/selectivity for the three systems is in the order of ethanol < IPA < tert-butyl alcohol. Accordingly, it can be concluded that the larger the molecular size, the higher is the separation factor that can be achieved. The other factor helping P84™ to have a superior separation factor/selectivity for the pervaporation dehydration of aqueous IPA and tert-butyl alcohol mixtures is its small interstitial space among P84™ polymer chains, which can effectively discriminate molecules with different sizes. Accordingly, P84™ is a particularly advantageous copolymer for separating higher

molecular sized organic liquids, in particular, those comprising organic compounds with 3 or more carbons.

When comparing P84TM with MatrimidTM manufactured by Ciba-Geigy Specialty Chemicals (another popular commercial polyimide), the d-space of the former is much less than that of the latter, i.e., 5.36 Å vs 6.72 Å.[1]

Advantageously, P84TM membranes can achieve a much better selectivity than Matrimid membranes for the dehydration of aqueous tert-butyl alcohol and IPA solutions.

When comparing membrane performance in flux, Figure 2 shows that the ethanol/water mixture has the lowest flux, followed by the IPA/water mixture and the tert-butyl alcohol/water mixture. The trend is instinctively contrary to the sorption data and molecular size of different alcohols. However, the flux cannot reflect the intrinsic separation properties of a membrane because it is a combination of membrane permeance and the driving force (partial pressure difference across the membrane) as discussed in the previous literature.[1],[3][5]

Figure 3 replots the data in terms of water permeance and alcohol permeance. The water permeance (close to total permeance due to a very small amount of alcohol permeance) of three alcohol systems follows the reverse order of flux, i.e., ethanol > IPA > tert-butyl alcohol. This is consistent with the highest sorption of membrane in the ethanol/water system and the faster diffusion rate of ethanol. This again supports the view that permeance is a more meaningful tool than flux when we investigate membrane intrinsic properties.[5],[3],[7]

Clearly, in accordance with alcohols' physicochemical properties, Figure 3 also indicates that the order of alcohol permeance is as follows: ethanol > IPA > tert-butyl alcohol.

To simulate the membrane status and investigate P84TM molecular changes under high operating temperatures, dense P84TM membranes were immersed in three closed containers containing 85 wt % various alcohol solutions at 100 °C for about 10 h; these membranes were then immediately tested by XRD and DSC.

The XRD spectra shown in Figure 4 clearly illustrate that the peaks of membranes immersed in aqueous alcohol solutions shift to the left compared to the original dense film. This indicates that P84TM membrane swells in these solutions and the swelling makes the interstitial space of polymer chains increase. Additionally, the peak of membranes immersed in the ethanol/water solution significantly differs from the peaks of membranes immersed in IPA/ water and tert-butyl alcohol/water solutions. This reveals that the d-space of the membrane in the ethanol/water solution expands greatly compared to those in the

other two solutions. The strong membrane swelling in ethanol/water is due to the smaller molecular size, the higher linearity of ethanol (as indicated by the quasi-aspect ratio in Table 3), and the strong affinity between ethanol and P84™. As a result, P84™ membranes have higher water and ethanol permeability but lower selectivity.

DSC results shown in Table 3 compare the glass transition temperatures (T_g) of membranes immersed in different aqueous solvent solutions at 100 °C for 10 hours. It is evident that all T_g 's shift to a lower temperature compared to that of the original dense film. The lowest T_g is observed for membranes in the ethanol/water solution, while membranes immersed in IPA/water and tert-butyl alcohol have similar T_g 's. These results suggest that the polymer chain mobility and free volume of P84™ membranes are severely affected by aqueous ethanol solutions but are not affected for aqueous IPA and tert-butyl alcohol solutions.

Table 3. Glass Transition Temperatures of P84™ original Dense Film and P84™ Dense Film Immersed in Various Alcohol Solutions.

alcohol/water mixtures	T_g (°C)
P84™ original dense film	317
ethanol/water	298
IPA/water	303
tert-butyl alcohol/water	303

It can be concluded that P84™ membranes can be significantly swollen by ethanol because of their strong affinity, as suggested by their close solubility parameters. XRD and DSC results confirm that P84™ undergoes significant swelling and chain relaxation in aqueous ethanol solutions at operating conditions. Consequently, both water permeance and ethanol permeance are the highest, while the selectivity is the lowest, among the three alcohol/water systems. On the other hand, these results surprisingly indicate that P84™ membranes exhibit impressive separation performance in 2-propanol/water and tert-butyl alcohol/water systems because of the small interstitial d-space in P84™ membranes, the lower affinity between IPA/tert-butyl alcohol and the membrane, the higher sorption selectivity, and the larger molecular sizes.

P84™ heat treated co-polymer membranes are therefore ideal for separating aqueous/organic liquid mixtures, wherein the organic compounds in the liquid mixture have 3 or more carbon atoms.

Example 2

A solution containing 25% P84™ co-polyimide, 65% N-methyl-2-pyrrolidone (NMP), and 10% acetone was mixed homogenously and filtered through a 5 micron filter. The solution was cast onto a glass plate using a casting knife with a set gap of 200µm. After about 10 seconds hot air blown followed by 10 seconds free evaporation, the film was immersed in a water coagulation bath at 25°C. The formed membrane was immersed in water overnight to remove residual solvents, then solvent exchanged by immersion into methanol three times, each time being for 1 hour, followed by immersion in 10wt% SYLGARD™ 184 in hexane solution three times, each time 1 hour. The membrane was dried in air naturally after solvent exchange.

A series of the above membranes were then treated in a vacuum oven at a rate of 0.6°C/min to different temperatures, held for 6hrs. The heat treated membranes and the original membrane were tested as flat sheet coupon at 55°C with around 85wt% IPA in water mixture. Results are shown in Table 4 below.

Table 4. Pervaporation performance of P84™ membranes at different heat treatment temperatures.

Heat treat Temperature (°C)	Testing Temperature (°C)	Feed water (wt%)	Permeate water (wt%)	Total Flux (g/m ² hr)	Separation factor (water /IPA)
0	55	15.2	70.9	2473.0	13.6
100	55	16	95.9	930.1	123
150	55	15.2	90.5	992.9	53.5
200	55	15.2	99.3	624.2	835.0
250	55	16.1	99.5	439.6	1051.2

Example 3

A P84™ membrane was prepared as in Example 2 with heat treatment in a vacuum at 250°C. The sample was tested with aqueous IPA solutions of different water content at 60°C. Results are recorded in Table 5 below. It is clear from the data in Table 5 that the membrane shows high selectivity to water at a broad water feed concentration range.

Table 5. Pervaporation performance at different feed water compositions

Feed water concentration (wt%)	Testing temperature T (°C)	Permeate water concentration (wt%)	Total flux (g/m ² h)	Separation Factor (water /IPA)
100.0	60	100	892	---
76.1	60	99.946	609	732
62.9	60	99.952	636	1096
41.7	60	99.949	583	3250
27.1	60	99.967	517	8248
9.2	60	99.925	300	13419

Example 4

A P84™ membrane was prepared as in Example 2 with heat treatment in a vacuum at 250°C. The sample was tested with 85wt% IPA solutions at 60-100°C. Results are recorded in Table 6 below. It can be seen that at higher temperatures, the membrane exhibits higher flux and higher separation factors.

Table 6. Pervaporation performance of P84™ membrane treated at 250°C at different operating temperatures

Testing temperature (°C)	Total flux (g/m ² hr)	Separation factor (water /IPA)
100	2030.6	5756
80	1039.6	4116
60	432.3	3866

Example 5

A P84™ membrane was prepared as in Example 2 with heat treatment in a vacuum oven at 100°C. The sample was tested with 85wt% IPA in water mixture at 60-100°C. Results are recorded in Table 7 below.

Table 7. Pervaporation performance of P84™ membrane treated at 100°C at different operating temperatures

Testing temperature (°C)	Total flux (g/m ² hr)	Separation factor (water /IPA)
100	5295.6	103.8
80	2454.6	125.9
60	1046.7	148

5

Example 6

An annealed P84™ membrane was prepared as in Example 2 with heat treatment in a vacuum oven at 250°C. The sample was tested with 85wt% ethanol water mixture from 60-100°C. Results are listed in Table 8 below.

10

Table 8. Pervaporation performance for ethanol (EtOH)/water mixture of P84™ membrane treated at 250°C at different operating temperatures

Testing temperature (°C)	Total flux (g/m ² hr)	Separation factor (water /EtOH)
100	1702.3	1112
80	900.7	1210
60	388.8	1393.5

Example 7

15

An annealed P84™ membrane was prepared as in Example 2 with heat treatment in a vacuum oven at 250°C. The sample was tested with 85wt% tert-butanol water mixture from 60-100°C. Results are listed in Table 9 below. A much higher separation factor was achieved for aqueous tert-butanol system than aqueous IPA and ethanol solutions because the larger size difference between water and tert-butanol molecules.

20

Table 9. Pervaporation performance for tert-butanol/water mixture of P84™ membrane treated at 250°C at different operating temperatures

Testing temperature (°C)	Total flux (g/m ² hr)	Separation factor (water /alcohol)
100	2125.6	9730
80	1112.2	9231
60	461	9382

Example 8

A solution containing 28% P84™ co-polyimide, 72% N-methyl-2-pyrrolidone (NMP) was prepared by the following procedure.

5 P84™ polymer powders were first dispersed in a cold NMP solvent (0-3°C) with a high speed stirrer. The low temperature slowed down the dissolution rate and prevented agglomeration of polymer powders. The solution was agitated until the polymer was fully dissolved. The bore fluid composition was 95/5 (w/w) mixture of NMP and water.

10 Tap water (26°C) was used as coagulant. Both polymer solution and bore fluid were extruded through a spinneret at room temperature with an air gap from 0 to 1.5 cm. The hollow fibers were stored in water for 3 days, then solvent exchanged by washing with methanol three times, each time 0.5 hour, followed by washing with 10wt% SYLGARD™ 184 in hexane solution three times, each time 0.5 hour. The hollow fibers were dried in air naturally after solvent exchange.

15 A series of the above membranes were then treated in a vacuum oven at a certain rate to different temperatures, hold for 1~2hrs. The heat treated membranes and the original membrane were tested at 60°C with 85wt% IPA in water mixture.

20 Results are shown in Table 10. The separation factor of membranes heat treated at 300°C is much higher than that of the prior art, while the flux is also very high when comparing membranes which have comparable separation factor in the prior art. Another example is that commercial flat sheet PERVAP 2510 membrane which is typically used for neutral solvent dehydration, such as IPA, has a performance of flux 857g/m²hr and separation factor of 1053 at 60°C with feed 85wt% IPA/water solution. The hollow fiber membranes heat treated at 250°C and 300°C exhibited comparable flux and much higher separation factor.

Table 10. Pervaporation performance of P84™ hollow fiber membranes before and after heat treatment

Membrane code	Air Gap (mm)	Without heat treatment		200°C heat treated		250°C heat treated		300°C heat treated	
		Flux (g/m ² hr)	Separation factor (water/IPA)	Flux (g/m ² hr)	Separation factor (water/IPA)	Flux (g/m ² hr)	Separation factor (water/IPA)	Flux (g/m ² hr)	Separation factor (water/IPA)
Sample 1	0	1160	138.9	1072	699.6	1034	654.5	802.8	2778
Sample 2	5	1442	128.3	1207	895.8	996	1173	814	6540
Sample 3	10	1298	81.9	1032	502.1	865	2688	783.4	4252
Sample 4	15	1625	78.0	1422	694.5	1114	1930	883.5	10584

Example 9

P84™ hollow fiber membranes were prepared as described in Example 8 but the coagulation bath temperature was 6°C.

A series of the above membranes were coated with 3wt% poly-dimethylsiloxane (Sylgard™ 184) in 10wt% SYLGARD™ 184 in hexane solution for 0.5 hour then cured in air at room temperature for 24 hrs. Results are listed in Table 11 below.

A thin layer silicone rubber coating is also helpful for reducing the defects and improving membrane performance.

Table 11. Pervaporation performance of P84™ hollow fiber membranes before and after coating

Membrane code	Air Gap (mm)	Before coating		After coating	
		Flux (g/m ² hr)	Separation factor (water/IPA)	Flux (g/m ² hr)	Separation factor (water/IPA)
Sample 5	0	928.2	106.8	758.3	353.2
Sample 6	5	810.4	72.7	575.6	456.5
Sample 7	10	630.4	82.7	377.8	568.5
Sample 8	15	1058	56.4	426.6	179

It will appreciated that the separation factor significantly increased on the membrane when the poly-dimethylsiloxane coating was applied.

Example 10

The pervaporation performance of different known polyimide membranes was assessed in order to compare the selectivity of the polyimide membranes with the treated P84™ co-polyimide of Example 2. Table 12 below lists the pervaporation performance of different polyimide membranes in aqueous solution.

Table 12

Membrane material	Feed & concentration	Operation T °C	Total permeate flux (g/m ² hr)	Separation factor	Membrane structure	Ref.
Comparative Membrane 1: PEI (Ultem 1000)	91wt% EtOH/water	37	200	8	Dense	[9]
Comparative Membrane 2: PEI-DW	87.6wt% IPA/water	25	36	173	Asymmetric	[10]
Comparative Membrane 3: Kapton-H	80wt% EtOH/Water	75	18.11	655		
Comparative Membrane 4: Kapton-H	90wt% EtOH/water	75	12.12	850		
Comparative Membrane 5: PMDA-ODA	90wt% EtOH/water	75	81.90	230		
Comparative Membrane 6: BPDA-ODA/DABA (8/2)	90wt% EtOH/water	75	18.49	1800		
Comparative Membrane 7: BPDA-ODA/DABA (6/4)	90wt% EtOH/water	75	23.23	1600		
Comparative Membrane 8: BPDA-ODA/DABA (4/6)	90wt% EtOH/water	75	68.2	150	Dense	[11]
Comparative Membrane 9: Polyimide PI2080	95vol% (~93wt%) EtOH/water	60	1000	~900	Asymmetric	[8]
Comparative Membrane 10: Polyimide prepared from BTDA/ODA	95vol% (~93wt%) EtOH/water	25	37	1300	Composite	[12]

Comparative Membrane 11: Polyimide from interfacial polymerization	90wt% EtOH/water	40	1700	240	Composite	[13]
Comparative Membrane 12: Polyimide prepared by dip coating	95vol% (~93wt%) EtOH/water	60	600	550	Composite	[14]
Comparative Membrane 13: BHTDA-DBAPB	90wt% EtOH/water	55	650	50	Asymmetric	[15]
Comparative Membrane 14: Polyetherimide (Utem 1000) by cataphoretic electrodeposition	85wt% EtOH/water	40	65	50	Composite	[16]
Treated P84: Copolyimide	85wt% EtOH/water	60	388.8	1393	Asymmetric	
	85wt% IPA/water	60	432.3	3866		
	85wt% T-buOH/water	60	461	9382		
Treated P84: Copolyimide	85wt% IPA/water	60	883.5	10584	Hollow fiber	

EtOH: ethanol, IPA: isopropanol, T-buOH: tert-butanol.

It can be clearly seen from Table 12 that the treated P84 copolyimide of the present invention has superior selectivity over known polyimide membranes that are currently available commercially. Furthermore, the treated P84 copolyimide has superior flux over those of the known prior art or, alternatively, a relatively high flux with better selectivity.

Applications

Advantageously, the disclosed method produces a coated treated asymmetric membrane with an ultra-thin selective layer which has enhanced selectivity and permeability over membranes that have not been treated. Furthermore, the coated treated
5 membrane is a thin, substantially defect-free, selective membrane layer.

Advantageously, the disclosed method produces a selectively permeable membrane that can be used to separate organic compounds having at least three carbon atoms from aqueous liquids whilst avoiding problems associated with swelling of the membrane over prolonged time exposure to the organic compounds. This is particularly advantageous as
10 the membrane can be used for azeotropic mixtures such as water and isopropanol.

Advantageously, the disclosed method produces a selectively permeable membrane that is capable of separating higher alcohols, such as isopropanol, butanol, pentanol, etc, without undue swelling of the treated P84 copolyimide. Accordingly, membranes of the disclosed method produces membranes that are ideal candidates for pervaporation of
15 aqueous solutions of alcohols having three or more carbon atoms.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

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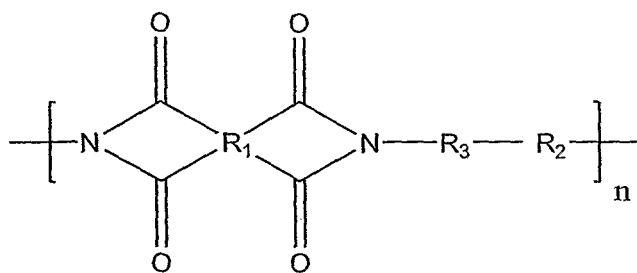
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Claims

1. A method of treating a permeable membrane comprising the steps of:

(a) providing a permeable membrane comprising a copolymer having (n)

5 repeating units of general formula (I):



(I)

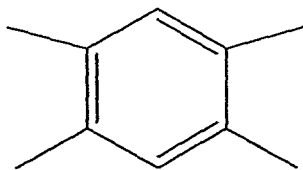
wherein R_1 and R_2 are aromatic hydrocarbon moieties, and

R_3 is an optional moiety and is selected from the group consisting of alkyls and
10 aromatic hydrocarbons;

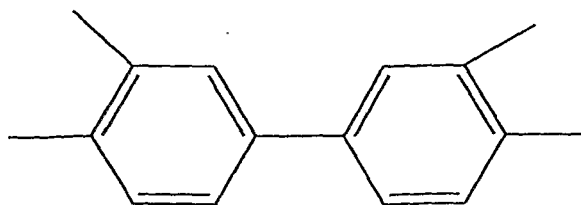
(b) heating said permeable membrane for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating; and

(c) forming a permeable sealant layer on at least one side of said membrane.

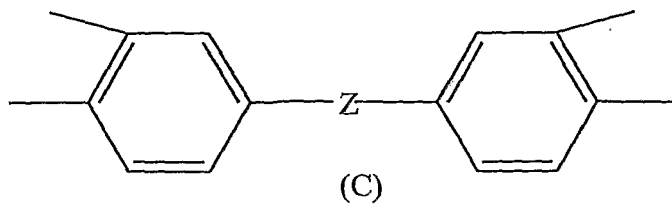
2. A method as claimed in claim 1, wherein the R_1 moiety is of composition selected from the group consisting of formula (A), formula (B), formula (C) and mixtures thereof,



(A)

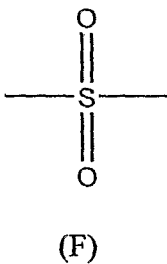
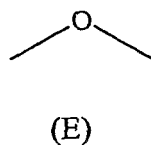
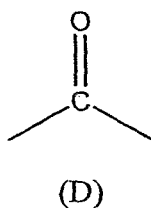


(B)

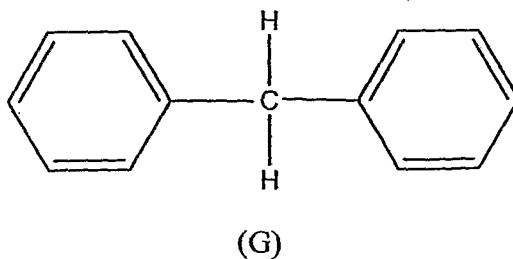


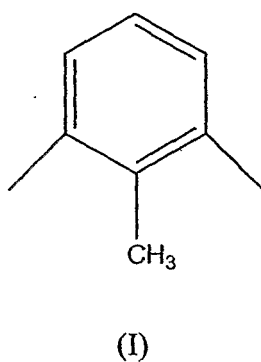
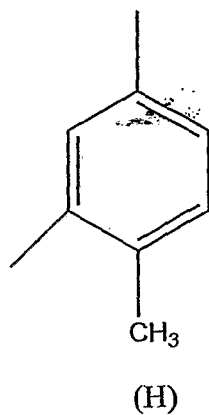
wherein Z is a moiety selected from the group consisting of ethers, epoxides, esters, carbonyls sulfonyls and mixtures thereof.

- 5
3. A method as claimed in claim 2, wherein Z has a composition selected from the group consisting of formula (D), formula (E), formula (F) and mixtures thereof,

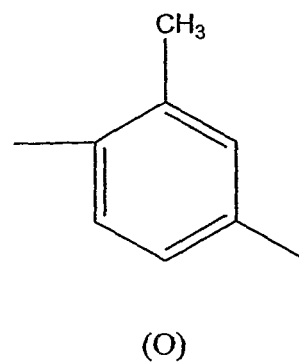
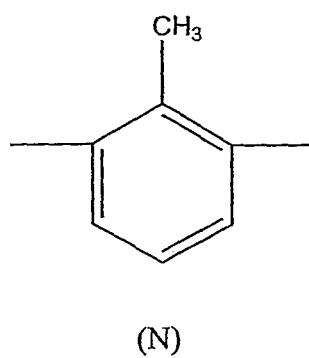
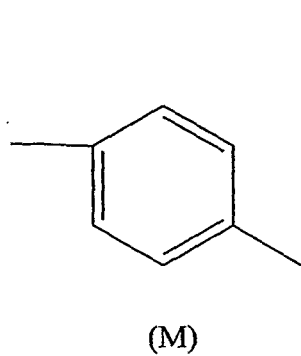
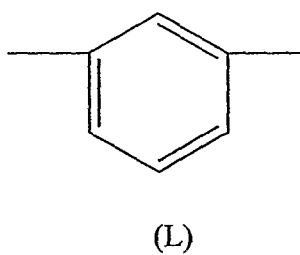
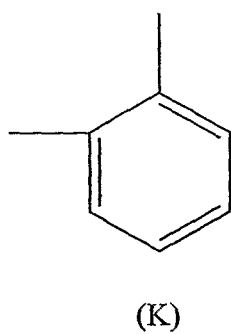
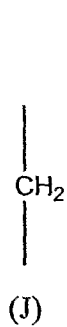


- 10
4. A method as claimed in claim 3, wherein R₂ is a moiety of composition selected from the group consisting of formula (G), formula (H), formula (I) and mixtures thereof,
- 15





5. A method as claimed in claim 1, wherein R_3 is a moiety of composition selected from the group consisting of formula (J), formula (K), formula (L), formula (M), formula (N), formula (O) and mixtures thereof,



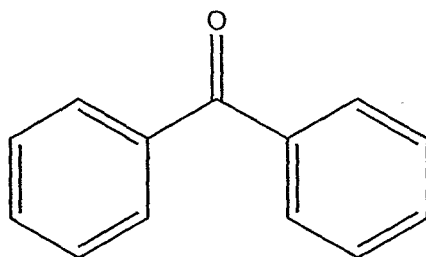
6. A method as claimed in claim 1, wherein said heating step (b) comprises the step of:

(b1) heating said permeable membrane at a temperature in the range selected from the group consisting of: 60°C to 400°C, 100°C to 400°C, 150°C to 400°C, 200°C to 400°C and 200°C to 350°C.

7. A method as claimed in claim 1, wherein said heating step (b) comprises the step of:

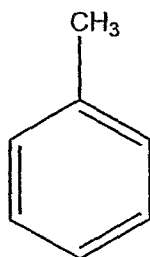
(b1) heating said permeable membrane for a time selected from the group consisting of 1 minute to 1500 minutes, 100 minutes to 1500 minutes, 250 minutes to 1500 minutes, 350 minutes to 1500 minutes, 500 minutes to 1500 minutes, 1000 minutes to 1500 minutes.

8. A method as claimed in claim 1, wherein R₁ has the composition of formula (P)



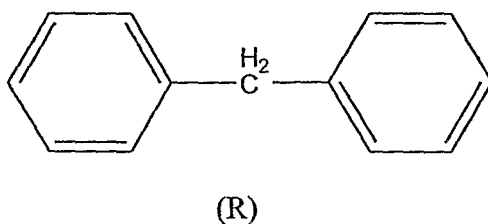
(P)

9. A method as claimed in claim 1, wherein R₃ has the composition of formula (Q)



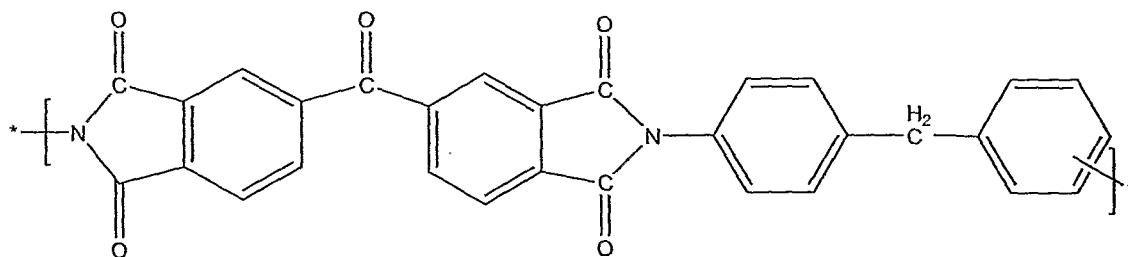
(Q)

10. A method as claimed in claim 1, wherein R_2 has the composition of formula (R)

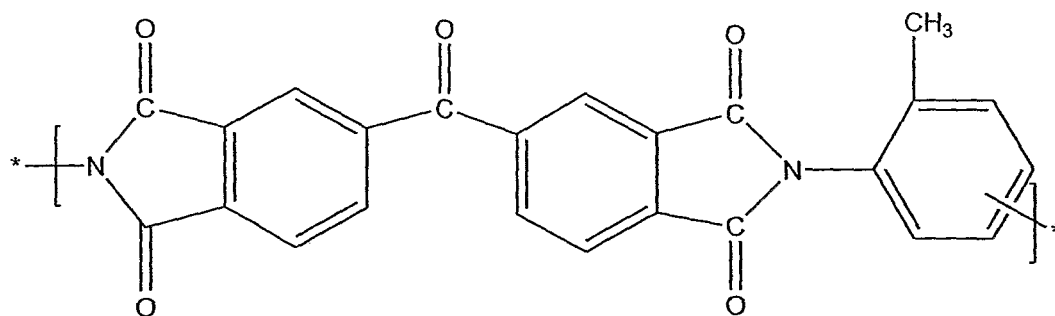


11. A method as claimed in claim 1, wherein said providing step (a) comprises the step of:

(a) providing a permeable membrane comprising a copolyimide polymer having (n) repeating units, wherein between 10% to 90% of said imide linkages having the following structural formula (IV):



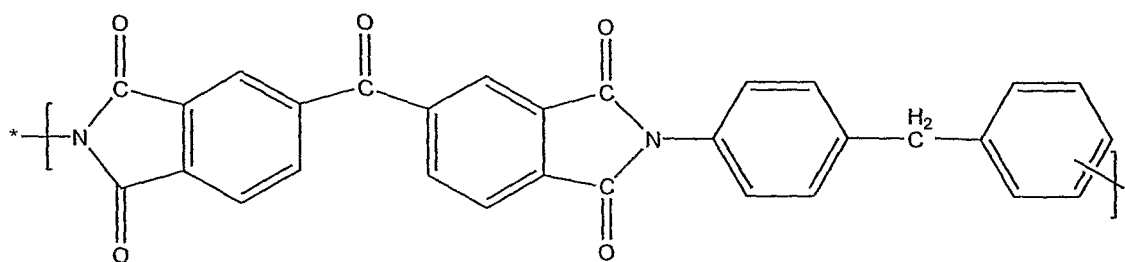
and wherein the remainder have imide linkages having the following structural formula (V):



12. A method as claimed in claim 1, wherein said providing step (a) comprises the step of:

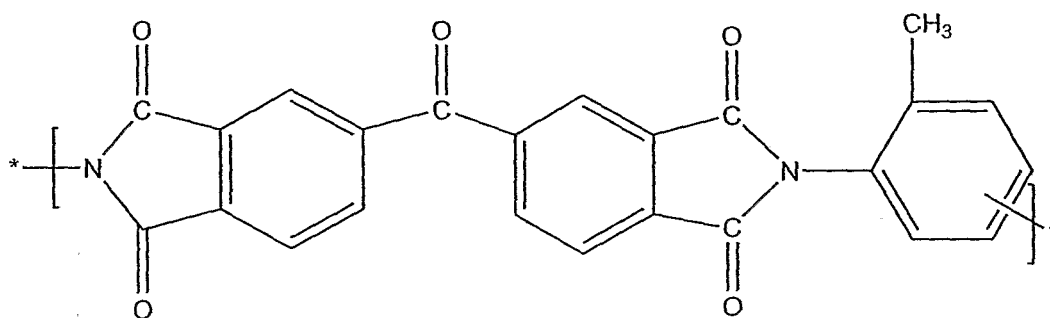
(a) providing a permeable membrane comprising a copolyimide polymer having (n) repeating units, wherein between 10% to 30% of said imide linkages having the

5 following structural formula (IV):



(IV)

and wherein the remainder have imide linkages having the following structural formula (V):



(V)

13. A method as claimed in claim 1, wherein said forming layer (c) comprises the step of:

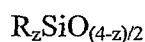
(c1) forming a water-permeable layer on said at least one side of said membrane. selected from the group consisting of polysiloxanes, copolymers of dimethylsiloxane and phenylenesilane; copolymers of dimethylsiloxane and polyurethane; organopolysiloxane/polycarbonate copolymers; polyvinylpyridines and copolymers thereof.

14. A method as claimed in claim 1, wherein the forming step (c1) comprises the step of:

(c2) forming a water-permeable silicone elastomer layer on said at least one side of said membrane.

5

15. A method as claimed in claim 14, wherein the silicone elastomer is an organopolysiloxane having the following average compositional formula:



10

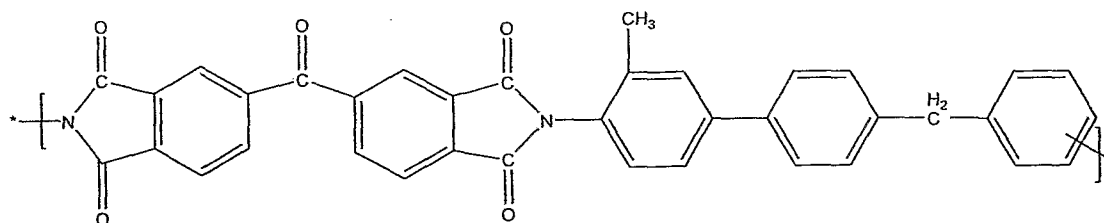
wherein the letter z is a positive number from 1.98 to 2.02

R_z is a substituted or unsubstituted aliphatic hydrocarbon of 1 to 12 carbon atoms or 1 to 6 carbon atoms.

16. A method as claimed in claim 15, wherein the organopolysiloxane is selected from the group consisting of dimethylpolysiloxane, methylphenylpolysiloxane, and copolymers thereof.

17. A method as claimed in claim 1, wherein the copolymer is of the following structural formula (VI):

20



(VI)

18. A membrane separation process for separating mixtures of fluids having at least a two fluid components that permeate through a membrane at different rates, the process comprising the steps of:

(c) providing a two-sided treated selectively permeable membrane made in the method of claim 1;

(d) contacting a first side of the membrane with a feed mixture comprising said mixtures of fluids; and

(e) causing the feed mixture to selectively permeate through the membrane and thereby form, on the second side of the membrane, a permeate

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composition which has a concentration of one of the fluid components that is greater than that of the feed mixture.

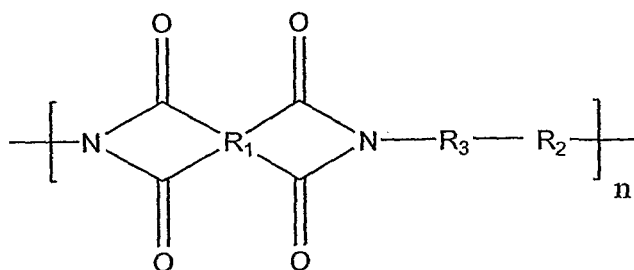
19 A membrane separation process as claimed in claim 18, wherein said feed mixture comprises an aqueous liquid and an organic liquid comprising compounds having at least three carbon atoms.

20. A membrane separation process as claimed in claim 19, wherein the organic liquid is selected from the group consisting of alcohols, ketones, aromatic hydrocarbons, aliphatic unsaturated hydrocarbons, ethers, esters, cycloaliphatic hydrocarbons, and mixtures thereof.

21. A membrane separation process as claimed in claim 19, wherein aqueous liquid comprises water and the organic liquid is an alcohol selected from the group consisting of saturated aliphatic alcohols having a carbon atom of between 3 to 8, unsaturated aliphatic alcohols having a carbon atom of between 3 to 8, alicyclic alcohols having a carbon atom of between 3 to 8, aromatic alcohols having a carbon atom of between 3 to 8, heterocyclic alcohols having a carbon atom of between 3 to 8 and mixtures thereof.

22. A membrane separation process for separating a mixture of an aqueous liquid and an organic liquid comprising compounds having at least three carbon atoms, the membrane separation process comprising the steps of:

(a) providing a permeable membrane comprising a copolymer having (n) repeating units of general formula (I):



(I)

wherein R_1 and R_2 are aromatic hydrocarbon moieties,

R_3 is an optional moiety and is selected from the group consisting of alkyls and aromatic hydrocarbons, and

wherein said permeable membrane has undergone heat treatment for a period of time to increase the selectivity of the permeable membrane relative to a membrane that has not undergone heating;

(b) providing, on a first side of the membrane, a feed mixture comprising said
5 mixtures of aqueous liquid and organic liquid; and

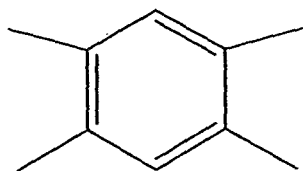
(c) causing the feed mixture to selectively permeate through the membrane and thereby form, on the second side of the membrane, a permeate composition which has a lower organic liquid concentration than that of the feed mixture.

10 23. A process as claimed in claim 22, wherein said feed mixture comprises an aqueous liquid and an organic liquid comprising compounds having at least three carbon atoms.

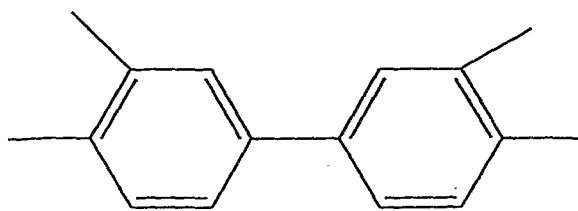
15 24. A process as claimed in claim 22, wherein the organic liquid is selected from the group consisting of alcohols, ketones, aromatic hydrocarbons, aliphatic unsaturated hydrocarbons, ethers, esters, cycloaliphatic hydrocarbons, and mixtures thereof.

20 25. A process as claimed in claim 24, wherein aqueous liquid comprises water and the organic liquid is an alcohol selected from the group consisting of saturated aliphatic alcohols having a carbon atom of between 3 to 8, unsaturated aliphatic alcohols having a carbon atom of between 3 to 8, alicyclic alcohols having a carbon atom of between 3 to 8, aromatic alcohols having a carbon atom of between 3 to 8, heterocyclic alcohols having a carbon atom of between 3 to 8 and mixtures thereof.

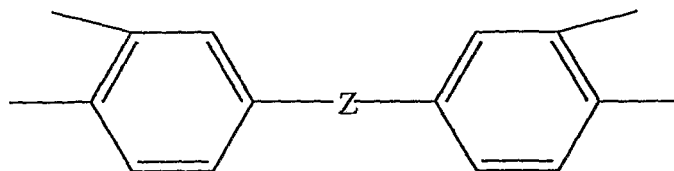
25 26. A process as claimed in claim 22, wherein the R_1 moiety is of composition selected from the group consisting of formula (A), formula (B), formula (C) and mixtures thereof,



(A)



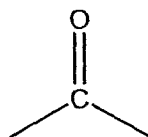
(B)



(C)

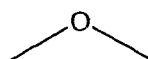
wherein Z is a moiety selected from the group consisting of ethers, epoxides,
 5 esters, carbonyls sulfonyls and mixtures thereof.

27. A process as claimed in claim 26, wherein Z has a composition selected from the
 group consisting of formula (D), formula (E), formula (F) and mixtures thereof,

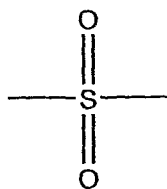


(D)

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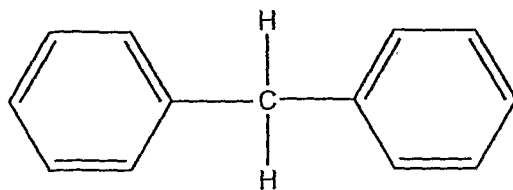


(E)

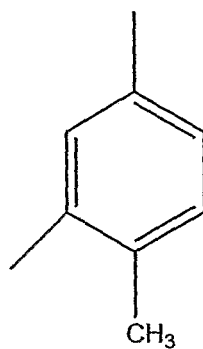


(F)

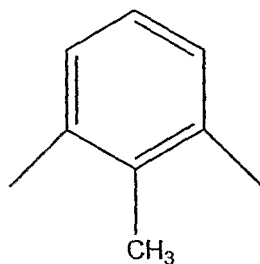
15 28. A process as claimed in claim 27, wherein R₂ is a moiety of composition selected
 from the group consisting of formula (G), formula (H), formula (I) and mixtures thereof,



(G)



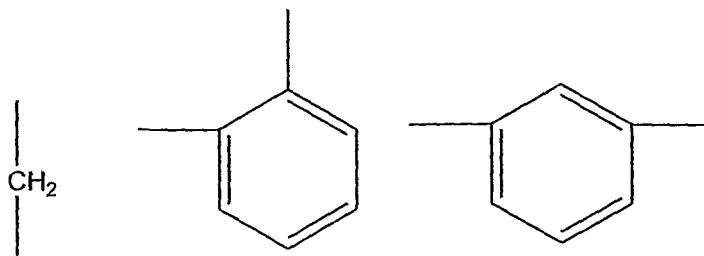
(H)



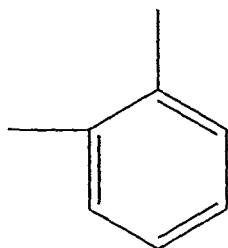
(I)

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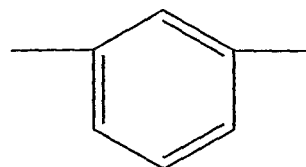
29. A process as claimed in claim 22, wherein R_3 is a moiety of composition selected from the group consisting of formula (J), formula (K), formula (L), formula (M), formula (N), formula (O) and mixtures thereof,



(J)

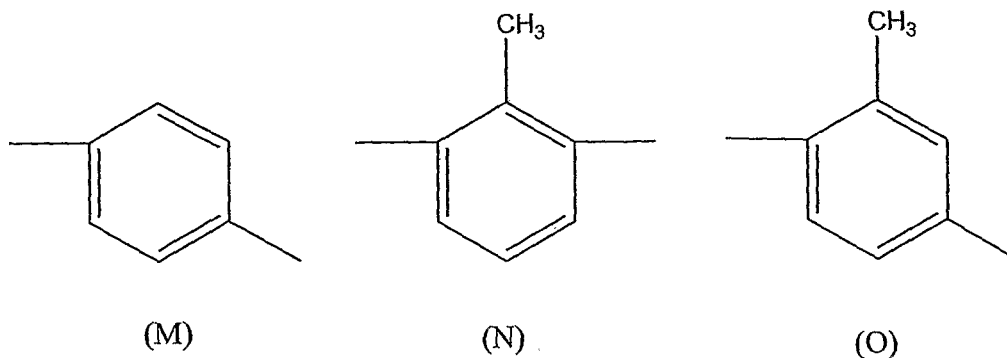


(K)



(L)

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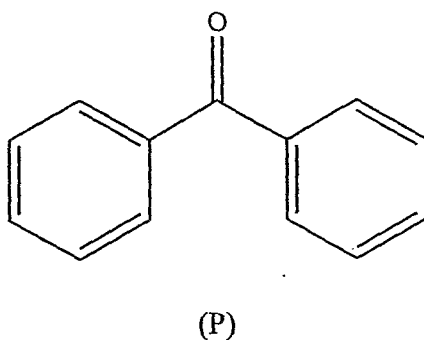
30. A process as claimed in claim 22, wherein said heating step (b) comprises the step of:

5 (b1) heating said permeable membrane at a temperature in the range selected from the group consisting of: 60°C to 400°C, 100°C to 400°C, 150°C to 400°C, 200°C to 400°C and 200°C to 350°C.

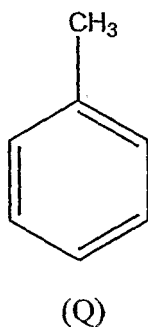
31. A process as claimed in claim 22, wherein said heating step (b) comprises the step of:

10 (b1) heating said permeable membrane for a time selected from the group consisting of 1 minute to 1500 minutes, 100 minutes to 1500 minutes, 250 minutes to 1500 minutes, 350 minutes to 1500 minutes, 500 minutes to 1500 minutes, 1000 minutes to 1500 minutes.

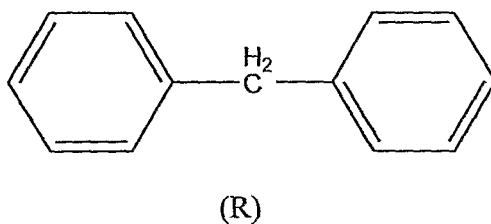
32. A process as claimed in claim 22, wherein R_1 has the composition of formula (P)



33. A process as claimed in claim 22, wherein R₃ has the composition of formula (Q)



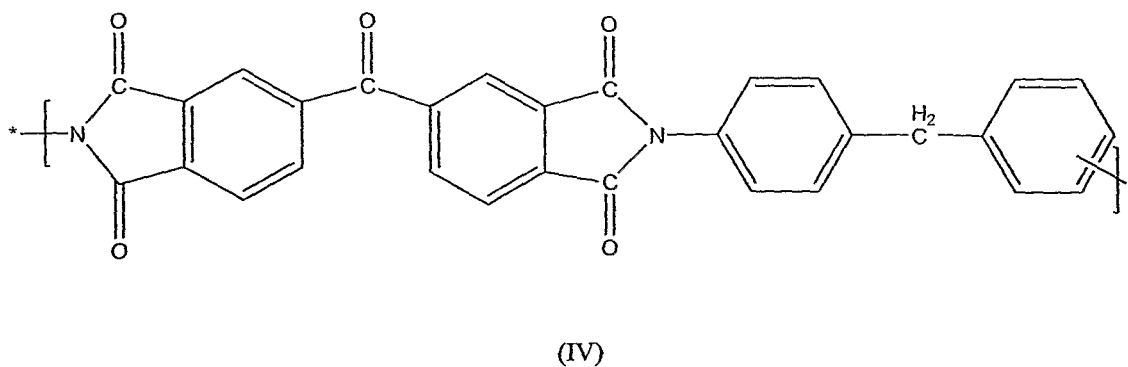
34. A process as claimed in claim 22, wherein R₂ has the composition of formula (R)



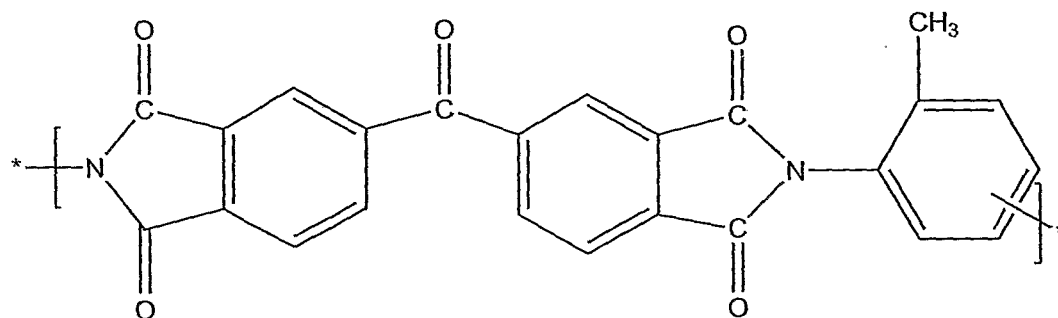
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35. A process as claimed in claim 22, wherein said providing step (a) comprises the step of:

- 10 (a) providing a permeable membrane comprising a copolyimide polymer having (n) repeating units, wherein between 10% to 90% of said imide linkages having the following structural formula (IV):



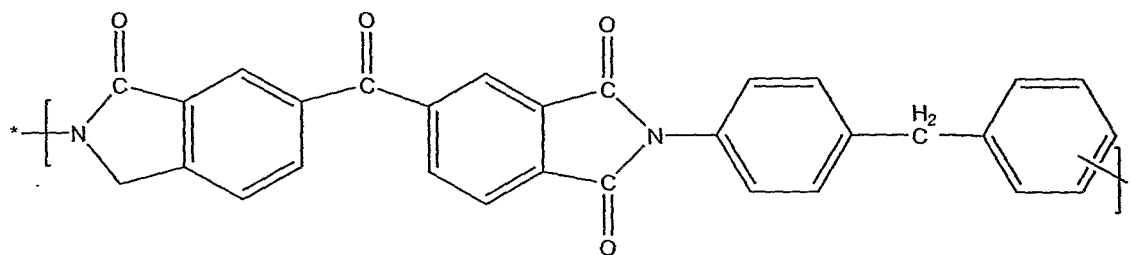
- 15 and wherein the remainder have imide linkages having the following structural formula (V):



(V)

36. A process as claimed in claim 22, wherein said providing step (a) comprises the step of:

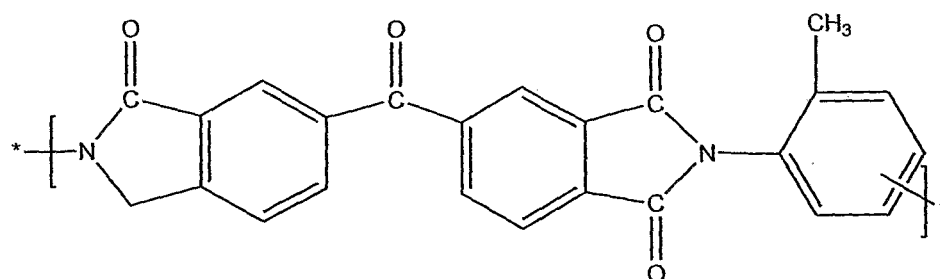
- 5 (a1) providing a permeable membrane comprising a copolyimide polymer having (n) repeating units, wherein between 70% to 90% of said imide linkages having the following structural formula (IV):



(IV)

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and wherein the remainder have imide linkages having the following structural formula (V):

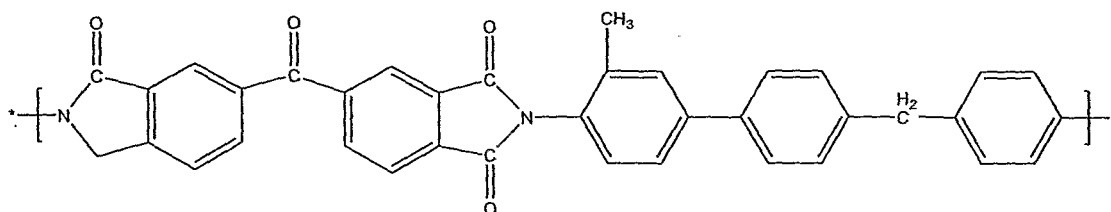


(V)

37. A process as claimed in claim 22, wherein said forming layer (c) comprises the step of:

(c1) forming a polysiloxane layer on at least one side of said membrane.

5 38. A process as claimed in claim 22, wherein the copolymer is of the following structural formula (VI):



(IV)

39. A process as claimed in claim 22, comprising the step of:

10 (d) heating said feed mixture to cause one of said aqueous liquid to form a vapor and permeate through said membrane.

40. A process as claimed in claim 39, comprising the step of:

15 (e) removing, from the second side of the membrane, said vapor that has permeated through said membrane.