

CLAIMS

1. A polymeric semipermeable membrane comprising a non-cross-linked base polymer having reactive pendant moieties, said base polymer being modified by forming a cross-linked skin onto a surface thereof, said skin being formed by a cross-linking reaction of reactive pendant moieties on said surface with an oligomer or another polymer thereby, said base polymer is covalently bonded to said oligomer or another polymer; wherein said base polymer is polyacrylonitrile (PAN) such that at least one portion of said cross-linked skin is covalently bonded to a nanofiltration (NF) layer by immersion of said cross-linked skin of said base polymer in polyethylenimine (PEI) and condensate solution comprising cyanuric chloride and sulfanilic acid thereby, said polymeric semipermeable membrane having acid and organic solvent stability, wherein said nanofiltration layer comprises:

- a. at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and
- b. at least one multifunctional amine having a molecular weight in the range of 400 to 750,000,

provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

2. The polymeric semipermeable membrane according to claim 1, wherein additionally comprising a woven or non-woven textile substrate underlying said base polymer.

3. The polymeric semipermeable membrane according to claim 1, wherein said base polymer is selected from the group consisting polyacrylonitrile polymer and any copolymers thereof.

4. The polymeric semipermeable membrane according to claim 1, wherein said base polymer preferably comprises polyacrylonitrile.

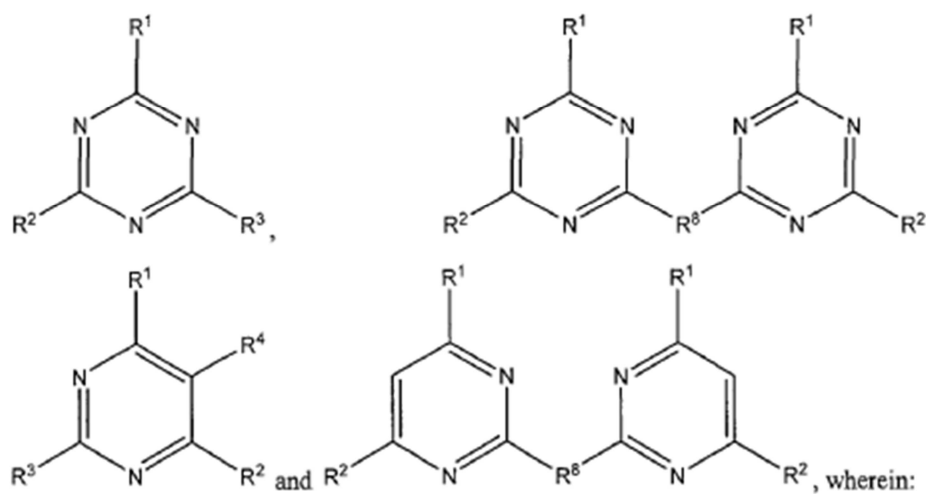
5. The polymeric semipermeable membrane according to claim 1, wherein said another polymer is selected from polyethylenimine, polyvinyl alcohol and a combination thereof.

~~6. The polymeric semipermeable membrane according to claim 1, wherein said another polymer is preferably polyethylenimine.~~

~~76. The polymeric semipermeable membrane according to claim 1, wherein said polymeric semipermeable membrane is an ultrafiltration (UF) membrane or a microfiltration (MF) membrane.~~

~~87. The polymeric semipermeable membrane according to claim 1, wherein said polymeric semipermeable membrane is a polyacrylonitrile ultrafiltration membrane and said another polymer is polyethylenimine.~~

98. The polymeric semipermeable membrane of claim 1, wherein said diazine or triazine-containing monomer or oligomer is selected from the group consisting of



R¹ is independently selected at each occurrence from bromo, chloro, iodo, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R² is independently selected at each occurrence from bromo, chloro and fluoro;

R³ is independently selected at each occurrence from bromo, chloro, fluoro,

-NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl;

R⁴ is selected from H, bromo, chloro, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R⁸ is independently at each occurrence -NH-A-NH-, wherein A is selected from C₁₋₂₀ aliphatic moieties, C₆₋₁₀ aromatic moieties, and combinations thereof; provided that at least two occurrences, R¹, R², R³ and R⁴, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R¹ and R² on a single ring are Cl, at least one of R³ and R⁴ is not Cl.

109. The polymeric semipermeable membrane of claim 1, wherein said multifunctional amine has a molecular weight of in the range of 400 to 250,000.

110. The polymeric semipermeable membrane of claim 1, wherein said multifunctional amine is selected from the group consisting of polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, and amine-modified polyepihalohydrins.

111. The polymeric semipermeable membrane of any of claims 1 to 11, wherein further comprising supplemental cross-linker selected from the group consisting of 2,4,6-trichloro-s-triazine, 4,6-dichloro-2-sodium p-sulfoanile-s-triazine (4,6-dichloro-2-p-anilinesulfonic acid

sodium salt-s-triazine), 4,6-dichloro-2-diethanolamine-s-triazine and 4,6-dichloro-2-amino-s-triazine.

~~1312.~~ A method of forming a polymeric semipermeable membrane comprising the steps of: providing a non-cross-linked base polymer having reactive pendant moieties; ~~and effecting a cross-linking reaction between the~~cross-linking said reactive pendant moieties ~~on a surface of said base polymer with a solution comprising an oligomer or another polymer, thereby forming a cross-linked skin on said a surface of said base polymer; covalently bonding said cross-linked skin to a nanofiltration (NF) layer by immersing said cross-linked skin in a condensate solution comprising cyanuric chloride and sulfanilic acid, wherein said method additionally comprising steps of forming a nanofiltration (NF) layer over at least a portion of said cross-linked skin, wherein said nanofiltration layer comprises:~~

- a. at least one di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer, and
- b. at least one multifunctional amine having a molecular weight in the range of 400 to 750,000,

provided that at least one of the di-, tri- or tetra-halo substituted diazine or triazine-containing monomer, oligomer or polymer is not a di- or triazine monomer which is substituted only by Cl.

~~1413.~~ The method according to claim 13, wherein said step of forming further comprising step of covalently bonding said NF layer to said cross-linked skin.

~~1514.~~ The method according to claim 13, wherein said method additionally comprising step of providing said base polymer selected from the group consisting of polyacrylonitrile polymer and any copolymers thereof.

~~16.~~ The method according to claim 13, wherein said method additionally comprising step of providing said base polymer comprising polyacrylonitrile.

~~1715.~~ The method according to claim 13, wherein said method additionally comprising step of providing said another polymer selected from polyethylenimine and polyvinyl alcohol.

~~1816.~~ The method according to claim 13, wherein said method additionally comprising step of providing said another polymer comprising polyethylenimine.

~~1917.~~ The method according to claim 13, wherein said step of effecting said cross-linking reaction at a first elevated temperature utilizing a solution of said oligomer or another polymer.

~~2018.~~ The method according to claim 18, wherein said first elevated temperature is in the range of 50 - 100 °C.

~~2119.~~ The method according to claim 18, wherein said first elevated temperature in the range of 70 - 90 °C.

R⁴ is selected from H, bromo, chloro, fluoro, -NHR⁵, -OR⁵ and SR⁵, wherein R⁵ is independently selected at each occurrence from H, optionally substituted alkyl and optionally substituted aryl; and

R⁸ is independently at each occurrence -NH-A-NH-, wherein A is selected from C₁₋₂₀ aliphatic moieties, C₆₋₁₀ aromatic moieties, and combinations thereof; provided that at least two occurrences, R¹, R², R³ and R⁴, taken together, are selected from bromo, chloro and fluoro, and further provided that when both R¹ and R² on a single ring are Cl, at least one of R³ and R⁴ is not Cl.

| ~~29~~27. The method according to claim 13, wherein additionally comprising step of providing said multifunctional amine having a molecular weight of in the range of 400 to 250,000.

| ~~30~~28. The method according to claim 13, wherein additionally comprising step of selecting said multifunctional amine from the group consisting of polyethylenimine, polyvinylamine, polyvinylanilines, polybenzylamines, polyvinylimidazolines, and amine-modified polyepihalohydrins.

| ~~31~~29. The method according to any of claims 13 to 30, wherein additionally comprising step of providing supplemental cross-linker selected from the group consisting of 2,4,6-trichloro-s-triazine, 4,6-dichloro-2-sodium p-sulfoanile-s-triazine (4,6-dichloro-2-p-anilinesulfonic acid sodium salt-s-triazine), 4,6-dichloro-2-diethanolamine-s-triazine and 4,6-dichloro-2-amino-s-triazine.