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(71) Applicant: COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH [IN/IN]; Rafi Marg, New Delhi 110001 (IN).

(72) Inventors: GHOSH, Pushpito Kumar; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). SHARMA, Saroj; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). DINDA, Milan;

Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). SHARMA, Chiragkumar Rameshbhai; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). CHATTERJEE, Uma; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). KULSHRESHTHA, Vaibhav; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). GHOSH, Soumyadeb; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). MAKWANA, Babulal Surabhai; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). THAMPY, Sreekumaran; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN). DESALE, Girish Rajanikant; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002 (IN).

(74) Agent: NAIR, Manisha Singh; Lex Orbis, Intellectual Property Practice, 709/710, Tolstoy House, 15 - 17, Tolstoy Marg, New Delhi 110 001 (IN).

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(54) Title: A PROCESS FOR THE PREPARATION OF ANION EXCHANGE MEMBRANE



Fig.1:

(57) Abstract: The present invention describes process of preparation of inter-polymer film of p-methylstyrene-co-divinylbenzene and its conversion into anion exchange membrane through a greener route which dispenses with the use of chloromethyl ether. The membrane with polyethylene binder is shown to have equivalent or even superior performance to anion exchange membrane prepared from styrene-co-divinylbenzene/polyethylene through chloromethyl ether route.



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A PROCESS FOR THE PREPARATION OF ANION EXCHANGE MEMBRANE

Field of invention:

The present invention relates to a process for preparation of anion exchange membrane which is safe and convenient compared to conventional method. Particularly, this method relates to the preparation of quaternized anion exchange membranes (AEMs) via benzylic bromination of crosslinked methyl substituted aromatic polymer followed by amination and its application for water desalination. The developed anion exchange membrane exhibits significant desalination behavior and can be used for all applications where such ion exchange membranes are required.

Background of invention:

Anion exchanges are generally prepared by quaternization of crosslinked chloromethylated polystyrene-DVB polymeric film. The synthesis of intermediate halomethylated (chloromethylated) polystyrene-DVB membrane involves the use of carcinogenic chloromethyl ether (CME). The use of CME for AEM preparation is hazardous to health.

The article "A novel positively charged composite membrane for nanofiltration prepared from poly (2,6-dimethyl-1,4-phenyleneoxide) by in situ amine crosslinking" published in J. Memb. Sci., 215, 25–32 (2003), by Tongwen et. al., describes the preparation of anion exchange resin from linear engineering plastics poly(2,6-dimethyl- 1,4-phenylene oxide) (PPO) and its characterization. A base substrate made of aryl-brominated PPO polymers and a top layer made of benzyl- and aryl-brominated PPO polymers are taken together and subjected to *in-situ* amine crosslinking to obtain a membrane. The resultant membrane was characterized with pure water flux and rejection of electrolytes $MgCl_2$ and $NaCl$. The properties of the nanofiltration membrane are significantly affected by the type of brominated polymers of the top layer, the amination time, and the composition of amination medium.

The article “Anion Exchange Membranes by Bromination of Benzylmethyl-Containing Poly(sulfone)s”, published in *Macromolecules*, 43, 2349–2356, (2010), by Jingling Yan and Michael A. Hickner, discloses the properties of anion-conducting membranes synthesized by halomethylation and quaternization of benzylmethyl-containing poly(sulfone)s. The benzylmethyl moieties serve as precursors to cationic sites, are introduced during polymer synthesis, thereby circumventing post modification of the polymer by chloromethylation.

The article entitled “Fundamental studies of a new series of anion exchange membranes: Membranes prepared from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and pyridine”, published in *Journal of Membrane Science* 279 (2006) 200–208, by Ming Gong et.al., describes the anion exchange membranes containing pyridinium groups was prepared by quaternization of bromomethylated poly(2,6- dimethyl-1,4-phenylene oxide) (BPPO) membrane with pyridine. The prepared AEM showed relatively low IEC, high water content and low membrane potential, which was due to the erosion of pyridine during the amination reaction.

Reference may be made to an article by Blanc, G.L., published in *Bull. Soc. Chin., France*, 33, 313, (1923), wherein they disclosed that the halomethylated aromatic hydrocarbons and polymeric analogues are promising key intermediate for the synthesis of many valuable chemicals for targeted applications for both laboratory and industrial scale. The halomethylation reaction particularly, Lewis acid catalyzed chloromethylation of aromatic group is an important intermediates step in realizing polymeric materials.

The article entitled “Porogenic Solvents Influence on Morphology of 4-Vinylbenzyl Chloride Based PolyHIPEs”, published in *Macromolecules*, 41,3543-3546 (2008), by Peter Krajnc et.al., describes the poly(high internal phase emulsion) materials were prepared from concentrated emulsions containing 4-vinylbenzyl chloride as the reactive monomer and divinylbenzene as the cross-linker. The process of drying the polyHIPE materials also influenced the wet porosity. They have not attempted directly from methyl vinyl benzene.

The article entitled “A New Strategy to Microporous Polymers: Knitting Rigid Aromatic Building Blocks by External Cross-Linker”, published in *Macromolecules*, 44, 2410-2414 (2011), by Bien Tan et.al. They describes a series of microporous polymers via a low-cost versatile strategy, which involves “knitting” rigid aromatic building blocks, such as benzene, biphenyl, 1,3,5-triphenylbenzene, methylbenzene, chlorobenzene, and phenol using an external cross-linker. These materials are predominantly microporous and exhibit high surface areas. Moreover, different building blocks can generate materials with different pore structures, functional groups and application properties, which are significant for materials design. They used dimethoxymethane as linkers instead of CME.

Objects of the invention:

The main object of the present invention is to provide a process for preparation of anion exchange membrane.

Another object of the present invention is to prepare styrene-co-divinylbenzene (Sty-co-DVB) type polymeric anion exchange membranes bearing quaternary ammonium groups in safe and eco-friendly manner.

Another object of the present invention is to provide a process to avoid the use of hazardous chloromethyl ether (CME) for chloromethylation of the aromatic ring of styrene moiety to introduce a $-\text{CH}_2\text{Cl}$ group.

Yet another object of the present invention is to provide a process to recognize that bromomethyl group ($-\text{CH}_2\text{Br}$) would be even more efficient for quaternization.

Yet another object is to recognize that there is more than one way to introduce bromomethyl group ($-\text{CH}_2\text{Br}$) essential for quaternization.

Yet another object is to recognize that bromination of the methyl group of the polymer formed from *p*-methylstyrene (*p*-MS) and divinylbenzene (DVB) would result in such a bromomethyl group.

Yet another object is to undertake such bromination reaction directly on inter-polymer films prepared by casting and melt extrusion process.

Yet another object is to demonstrate such equivalence of performance through electro dialysis-based desalination, keeping the cation exchange membrane constant.

Summary of the invention

Accordingly, the present invention provides a process for the preparation of inter-polymer anion exchange membrane wherein the said process comprising the steps of:

- a) preparing an inter-polymer film of *p*-methylstyrene-co-divinyl benzene ((*p*-MS-co-DVB)/binder by adding *p*-methylstyrene as monomer, divinylbenzene as crosslinker, benzoyl peroxide as radical initiator either neat or into a solution of PVC in a solvent under stirring at temperature ranging between 60-70°C for a period ranging between 3-5 hrs in followed by pouring the said solution on a glass plate and casting subsequently drying at temperature ranging between 11-14 hrs at 25-35°C to obtain inter-polymer film;
- b) optionally, preparing an inter-polymer film by adding mixture of *p*-methyl styrene, divinylbenzene, benzoyl peroxide and toluene into melted mixture of binder under constant stirring at 80-95°C for a period ranging between 3-5 hrs followed by increasing the temperature ranging between 130-140°C to distill out the solvent from the polymer mixture to obtain noodles and cutting into small pellets subsequently keeping the said pellets in an oven at 75-80°C for a period ranging between 12-16 hrs and after curing converting pellets into inter-polymer film;
- c) benzylic halogenating the inter-polymer film as obtained in step (a) or (b) by treating inter-polymer film with a halogenations agent in mole ratio 1:1 to 2.5:1 in respect of *p*-methylstyrene, benzoyl peroxide and chlorinated solvent under stirring at temperature ranging between 75-80°C for a period ranging 5-10 hrs under photo irradiation to obtain halogenated inter-polymer film;

- d) providing quaternisation of halogenated inter polymer film as obtained in step (b) by to obtain inter-polymer anion exchange membrane

In an embodiment of the present invention binder used in step (b) is selected from the group consisting of polyethylene, chlorinated and fluorinated polymers, polycarbonate, polyester.

In one embodiment of the present invention polyethylene binder is selected from the group consisting of HDPE, LDPE, LLDPE or mixtures thereof.

In another embodiment of the present invention melted mixture of binder in step (b) is prepared by heating HDPE, LLDPE and xylene at temperature ranging between 140-160°C to melt PE and homogenise followed by adding toluene into PE melt and cooling the mixture at temperature ranging between 80-90°C to obtain melted mixture of binder.

Still in another embodiment of the present invention the films were of 0.1-0.3 mm thickness and contained 20-55% *p*-MS and 40-80% binder by weight.

Still in another embodiment of the present invention halogenation in step (c) at benzylic position involves chlorination or bromination or iodination and preferably bromination.

Still in another embodiment of the present invention bromination is carried out by N-bromosuccinimide or liquid bromine or 2:1 bromide-bromate.

Still in another embodiment of the present invention photoirradiation in step (c) is done by tungsten lamp, solar radiation, CFL lamp, LED lamp as light source.

Still in another embodiment of the present invention the degree of mono bromination of *p*-MS is 40-90%.

Still in another embodiment of the present invention the brominated film having 8-16% bromine by weight is quaternized employing tertiary amines and phosphines.

Still in another embodiment of the present invention the degree of quaternization is 80-100%.

Still in another embodiment of the present invention the membrane is conditioned prior to evaluation of membrane properties and membrane performance.

Still in another embodiment of the present invention Ion exchange membrane is having thickness of 0.1-0.3 mm, ion exchange capacity of 0.8-2.0 meq.g⁻¹ dry weight,

ionic resistance of 5-35 ohm.cm², water uptake of 5-25% by weight, and transport number of 0.85-0.98.

Still in another embodiment of the present invention Ion exchange membrane is found suitable for electrodialytic desalination and is used for all applications where such ion exchange membranes are used.

Brief description of the drawing

Fig 1: Picture of Mixtruder used for the preparation of *p*-MS-co-DVB/PE based inter-polymer

Fig 2: Picture of blow film extruder used for the preparation of *p*-MS-co-DVB/PE based inter-polymer film

Fig 3: TDS vs. time plot for desalination of brackish water of TDS 2000 mg/L using AEM-7 and AEM-8 with CEM at an applied potential 1.5 volt/cell pair in ED stack

Detailed description of the Invention:

The present invention relates to an improved process for the preparation of anion exchange membrane using two different approaches. The first approach relates to preparation of *p*-methylstyrene-co-divinylbenene (*p*-MS-co-DVB) polymer by radical polymerization with benzoyl peroxide (BPO) initiator in a solution additionally containing co-dissolved polyvinyl chloride (PVC), casting films from the above polymer solution carrying out benzylic bromination of the resultant polymeric film employing N-Bromosuccinimide(NBS) and thereafter subjecting the resultant film to amination to obtain quaternary ammonium sites. The second approach involves the preparation of inter-polymer film of *p*-MS-co-DVB polymer by radical polymerization with BPO through melt extrusion process with the mixture of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) and conversion of this inter-polymer into thin film through blow film extrusion. Thereafter, the resulting thin film was subjected to benzylic bromination and subsequent amination to get quaternary ammonium group. In this way, two different processes have been adopted to prepare anion exchange membrane by greener route by avoiding hazardous chloromethylether. The thickness and ion exchange capacities of the AEMs prepared by former process was the range of 0.15-0.17mm and 1.30-1.33 meq.g⁻¹ while, by later process theses were 0.24-0.28mm and 0.8-0.85 meq.g⁻¹ respectively.

Novel features of the Invention:

The main inventive steps involve the following:

1. Recognising that if *p*-methylstyrene-co-divinylbenzene (*p*-MS-co-DVB) type polymeric films are prepared and subjected to benzylic bromination then a bromomethyl group will get introduced which is similar to the chloromethyl group obtained when styrene-co-DVB polymer is treated with chloromethyl ether-conc. HCl.
2. Carrying out benzylic bromination directly on casted and blown extruded films.
3. Recognising further that bromomethyl group can be aminated more readily than chloromethyl group.
4. Recognizing further that *p*-methylstyrene (*p*-MS) as monomer may have better compatibility with polyethylene binder than styrene monomer which would lead to more uniform film and membrane prepared there from.

EXAMPLES

Following are the examples given to further illustrate the invention and should not be construed to limit the scope of the present invention.

Example 1

A mixture containing *p*-methylstyrene (5.60g), DVB (divinyl benzene)(1.40g), and benzoyl peroxide (BPO) as initiator (1%(w/w) with respect to monomer mixture) were added into a solution of PVC(3g) in 30 ml of tetrahydrofuron (THF) under constant stirring at 65°C for 4 hrs. The resultant hot solution was poured on a glass plate and a film was cast by 'SS-304' metal roller to get uniform thickness of the film in closed casting chamber. It was dried at 30°C for 12 hrs. Thereafter, the film was peeled off from the glass plate and un-reacted monomer and solvent were removed through washing with methanol prior to further functionalization.

Example 2

The experiment of Example-1 was repeated for the preparation of inter-polymer film by varying the composition of *p*-MS (5.95g) and DVB (1.05g), BPO (1%(w/w) with respect to monomer mixture), while keeping other parameter constant. The film was peeled off from the glass plate treated to remove unreacted monomer and solvent as similar method given in Example-1.

Example 3

The experiment of Example-1 was repeated to prepare the inter-polymer film by varying the composition of *p*-MS (6.3g) and DVB (0.70g), BPO (1% (w/w) with respect to monomer mixture) while keeping other parameter constant. The film was peeled off from the glass plate and treated to remove unreacted monomer and solvent as similar method given in Example 1.

Example 4

This example pertains to experiments on benzylic bromination of the inter-polymer films of examples 1-3. N-bromosuccinimide (NBS), (NBS: *p*-MS = 2.5:1 w/w) and BPO (BPO: *p*-MS = 0.02 (w/w)) were added into 800 ml of pure and mixed chlorinated solvents (CCl₄; DCE; varying proportions of CCl₄ + DCE) and the solution poured into a cylindrical glass reactor. The inter-polymer films were allowed to react in immersed solution for 6 h at 80°C under constant stirring in the presence of a 100 W tungsten lamp. The brominated films were then removed, washed with methanol and dried under ambient conditions. It was further dried under vacuum (5 mm Hg Exact value) at 30°C and its Br-content was analyzed by Volhard method.

Example 5

This example pertains to the quaternization of brominated films of example-4. The films were immersed in aqueous trimethylamine solution (30% w/w) in closed container at 30°C for 24 h. The contents were occasionally shaken. The resultant membrane was washed thoroughly with water to remove the adhering amine. It was thereafter conditioned by immersing in 100ml 1 M HCl followed by water wash till neutral pH obtained, followed by immersing in 100 ml 1 M NaOH, followed by water

wash till once again neutral pH obtained. This cycle was repeated three times. The films were then kept standing in 100 ml 0.1 M NaCl solution for 24 h at 30°C. The adhering liquid on the membrane surface was wiped prior to measurement of membrane properties. (Table 1 and 2)

Table 1: Preparation of anion exchange membrane (AEMs) of *p*-MS-co-DVB/PVC film:

S. No.	solvent	Br content after bromination / % (w/w)	IEC of quaternized film (AEM)/ (meq.g ⁻¹) of dry membrane	R'' of quaternized film (AEM)/ (Ωcm^2) ^b	WU by AEM/ (%)	Remarks
1.	CCl ₄	6.13	1.00 (AEM-1)	2000	14	Stiff and non-uniform
2.	CCl ₄ /DCE (95:5 v/v)	12.2	1.33 (AEM-2)	4.00	22	flexible yet stable
3.	CCl ₄ /DCE (90:10 v/v)	10.4	1.20 (AEM-3)	7.00	24	Soft and poor strength
4.	DCE	12.7	1.50 (AEM-4)	4.00	16	Very weak strength

Table 2: Physicochemical and electrochemical properties of *p*-MS-co-DVB/PVC AEM

S. No.	<i>p</i> -MS (g)	DVB (g)	Film weight/ (<i>p</i> -MS content) g/(wt. %) ^a	NBS (g)	Bromine content in brominated film/ % Br(w/w)	IEC of quaternized film (AEM) (meq.g ⁻¹) of dry membrane	WU (%)
1.	6.30	0.70	7.0 (51.4)	14.25	12.0-12.2	(AEM-2)1.30-1.33	18-22
2.	5.95	1.05	7.4 (50.5)	13.46	9.10- 9.30	(AEM-5)1.00-1.02	14-15
3.	5.60	1.40	7.7 (48.8)	12.67	6.00-6.10	(AEM-6) 0.80-0.85	11-12

^aBinder weight was 3 g in all the films

Example 6

The granules of high density polyethylene (HDPE) (3.12 kg) and linear low density polyethylene (LLDPE) (0.780 kg) were added in a mixtruder (Fig.1). The xylene (1.25lit) was added into the mixture and the content was heated up to 150°C under stirring (through sigma blade) until mixture of PE melts and become homogeneous. Thereafter, 2.5 lit toluene was added into the mixture slowly and temperature of the reaction chamber was cooled down to 90°C. At this temperature the mixture of *p*-methylstyrene (2.0 lit), DVB (105ml), BPO (20g) and 500ml toluene were added into melted mixture of PE under constant stirring at 90°C. The polymerization was continued for 4 hrs. After polymerization the temperature of the chamber was increased to 140°C to distil out the solvent from the polymer mixture with in 30 minutes. After recovering approximately 85 % of the solvent from the polymer mixture, the inter-polymer of *p*-MS-co-DVB/PE was taken out from the reaction chamber in the form of noodles and cut into small pellets with the help of pelletizer.

Example 7

The inter-polymer pellets of example-6 were kept in oven at 80°C for 14 hrs to remove unreacted monomers and solvents. After curing, the inter-polymer pellets were converted into thin film of thickness 0.280mm through blow film extruder.

Example 8

This example pertains to experiments on benzylic bromination of the inter-polymer film of example 7. The *p*-MS-co-DVB/PE inter-polymer film was immersed in 500 ml of dichloro ethane at 30°C for 24 h to swell the film prior to the bromination reaction and reaction was carried out using NBS: *p*-MS ratio (1:1 molar basis) in DCE solvent for 10 h in a similar manner as given in example 4. Thereafter, the film was taken out from the reactor and washed and cleaned in similar manner given in example 4 and Br content was measured

Example 9

The quaternization of the brominated film of example 8 was carried out by the similar procedure given in example 5, except that the reaction temperature was 50°C instead of room temperature. The resultant membrane was washed with water to remove the

adhering amine and conditioned in similar way given in example 5. Thereafter, the ionic resistance and ion exchange capacity of this AEM was measured. (Table 3)

Table 3: Physicochemical properties of AEM based on *p*-MS-co-DVB/PE (AEM-7)

S No	<i>p</i> -MS content in pristine film/ % (w/w)	Br content of brominated film/ % (w/w);	IEC of quaternized film (AEM-7) (meq.g ⁻¹) of dry membrane	R ^m of AEM-7/ (Ωcm ²)	WU/ % w/w
1	1.792	8.00-8.30	0.80-0.96	25.0-35.0	5.30-7.80

Table 4: Physicochemical properties of AEM based on Sty-co-DVB/PE (AEM-8) and CEM (Cation exchange membrane) employed in the present studies

S. No.	Membrane	Thickness (d) (mm)	IEC (meq.g ⁻¹) of dry membrane	R ^m (Ωcm ²)	% WU in water
1	AEM- 8	0.15	1.40	9.00	7.30
2	CEM	0.17	1.90	8.00	6.10

Example 10

The EMF method was employed in the present study to estimate ($t_{Cl^-}^m$) for AEM-7 and AEM-8 using NaCl as electrolyte. The data are presented in Table 5. It can be seen that AEM-8 functionalized using CME and AEM-7 functionalized by the method of the present invention gave almost comparable transport numbers.

Table 5: Transport numbers computed from EMF method

S. No.	Membrane	EMF _{NaCl}	$[(t_{Cl^-}^m)_{EMF}]_{NaCl}$
1	AEM-7	0.495	0.948
2	AEM-8	0.507	0.958

Activity coefficient values of 0.798 and 0.922 were used for 0.1 M and 0.01 M NaCl solutions for computation of activities.

Example 11

ED experiments were performed in a laboratory-scale unit to assess the relative merits of AEM-7 and AEM-8 for the desalination of brackish water. Fig.3 shows the plot of TDS versus time for AEM-7 obtained by the method of the present invention and AEM-8 obtained by CME route. AEM-7 gave more efficient desalination, with a value of ca. 500 mg/L TDS being achieved within 60 min compared to 75 min for AEM-8. This invention shows that besides being a greener route, membrane homogeneity with better dispersion of ion exchange sites was achieved through use of *p*-methylstyrene in place of styrene.

Example 11

The Energy Consumption (EC) and Current Efficiency (CE) were obtained for AEM-7 and AEM-8. The data are presented in Table 6 shows that the values of EC and CE of AEM-7 developed in the present invention are marginally superior to the AEM-8. The EC was the lowest for AEM-7 while CE was the highest.

Table 6: EC and CE data for the AEM-7 and AEM-8

S No	AEM used in ED unit	EC (kWh/kg)	CE (%)
1	AEM-7	0.680	96.1
2	AEM-8	0.723	95.7

Example 12

The IEC values of the membranes remained nearly identical for three cycles of regeneration. The IEC values were also checked after ED experiments and no significant differences were seen. Stability of the AEMs under thermal and oxidative conditions is also important for their practical application in electrochemical processes. After Fenton's test, the IEC and membrane weight showed a reduction while R^m increased. The data are tabulated in Table 8. It can be seen that the data of

the AEM-7 is matched closely those of AEM-8. Both the membranes were also found to be hydrolytically stable.

Table 7: Percent reduction in IEC and weight, and increase in R_m of AEMs after subjecting to Fenton's test

S No	AEM used in ED unit	% reduction in IEC	% reduction in weight	% increase in R_m
2	AEM-7	0.69-0.75	1.2-1.4	0.30-0.60
3	AEM-8	0.81-1.00	1.5-1.8	0.50-0.90

ADVANTAGES OF THE INVENTION

1. The main advantage of the invention is that it makes the process of preparation of solution cast and blow extruded inter-polymer anion exchange membrane greener by dispensing with the use of chloromethyl ether.
2. Another advantage is that it enables such greening of the process without significant alteration in the operations and hence it may be more readily acceptable to membrane producers.
3. Another advantage is that although *p*-methylstyrene is costlier than styrene the overall impact on inter-polymer membrane cost is not substantial and such membranes should be cheaper than current commercial membranes.
4. Another advantage is that the invention teaches an even better performance in electrodialysis experiments when *p*-MS-co-DVB/PE-based anion exchange membrane of the present invention is used compared to the traditional styrene-co-DVB/PE-based anion exchange membrane, which improved is likely on account of better compatibility between the monomer and binder.
5. Another advantage is that the membrane stability is also seen to be marginally superior.

We Claim:

1. A process for the preparation of inter-polymer anion exchange membrane wherein the said process comprising the steps of:
 - a) preparing an inter-polymer film of *p*-methylstyrene-co-divinyl benzene ((*p*-MS-co-DVB)/binder) by adding *p*-methylstyrene as monomer, divinylbenzene as crosslinker, benzoyl peroxide as radical initiator either neat or into a solution of PVC in a solvent under stirring at temperature ranging between 60-70°C for a period ranging between 3-5 h in followed by pouring the said solution on a glass plate and casting subsequently drying at temperature ranging between 11-14 hrs at 25-35°C to obtain inter-polymer film;
 - b) optionally, preparing an inter-polymer film by adding mixture of *p*-methylstyrene, divinylbenzene, benzoyl peroxide and toluene into melted mixture of binder under constant stirring at 80-95°C for a period ranging between 3-5 hrs followed by increasing the temperature ranging between 130-140°C to distill out the solvent from the polymer mixture to obtain noodles and cutting into small pellets subsequently keeping the said pellets in an oven at 75-80°C for a period ranging between 12-16 hrs and after curing converting pellets into inter-polymer film;
 - c) benzylic halogenating the inter-polymer film as obtained in step (a) or (b) by treating inter-polymer film with a halogenations agent in mole ratio 1:1 to 2.5:1 in respect of *p*-methyl styrene, benzoyl peroxide and chlorinated solvent under stirring at temperature ranging between 75-80°C for a period ranging 5-10 hrs under photo irradiation to obtain halogenated inter polymer film;
 - d) providing quaternization of halogenated inter-polymer film as obtained in step (b) to obtain inter-polymer anion exchange membrane
2. A process as claimed in claim 1 wherein binder used in step (b) is selected from the group consisting of polyethylene, chlorinated and fluorinated polymers, polycarbonate, polyester.
3. A process as claimed in claim 2, wherein polyethylene binder is selected from the group consisting of HDPE, LDPE, LLDPE or mixtures thereof.

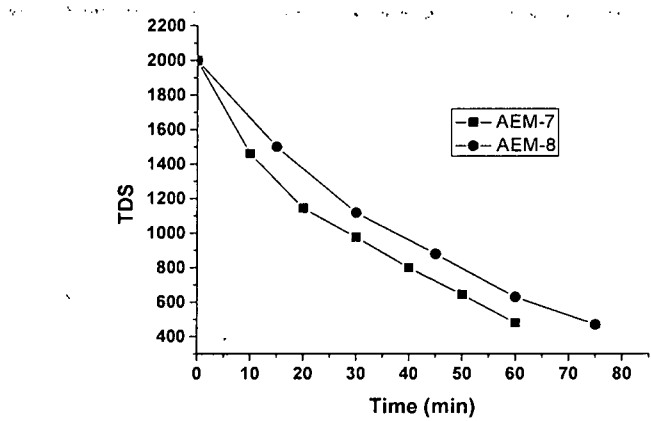
4. A process as claimed in claim 1, wherein melted mixture of binder in step (b) is prepared by heating HDPE, LLDPE and xylene at temperature ranging between 140-160°C to melt PE and homogenise followed by adding toluene into PE melt and cooling the mixture at temperature ranging between 80-90°C to obtain melted mixture of binder.
5. A process as claimed in claim 1, wherein the films were of 0.1-0.3 mm thickness and contained 20-55% *p*-MS and 40-80% binder by weight.
6. A process as claimed in claim 1, wherein halogenation in step (c) at benzylic position involves chlorination or bromination or iodination and preferably bromination.
7. A process as claimed in claim 6, wherein bromination is carried out by N-bromosuccinimide or liquid bromine or 2:1 bromide-bromate.
8. A process as claimed in claim 1, wherein photoirradiation in step (c) is done by tungsten lamp, solar radiation, CFL lamp, LED lamp as light source.
9. A process as claimed in claim 1, wherein the degree of monobromination of *p*-MS is 40-90%.
10. A process as claimed in claim 1, wherein the brominated film having 8-16% bromine by weight is quaternized employing tertiary amines and phosphines.
11. A process as claimed in claim 1, wherein the degree of quaternization is 80-100%.
12. A process as claimed in claim 1, wherein the membrane is conditioned prior to evaluation of membrane properties and membrane performance.
13. A process as claimed in claim 1, wherein Ion exchange membrane is having thickness of 0.1-0.3 mm, ion exchange capacity of 0.8-2.0 meq.g⁻¹ dry weight, ionic resistance of 5-35 ohm.cm², water uptake of 5-25% by weight, and transport number of 0.85-0.98.
14. A process as claimed in claim 1, wherein ion exchange membrane is found suitable for electrodialytic desalination and is used for all applications where such ion exchange membranes are used.



Fig.1:



Fig.2:



Applicant

Fig.3:

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2013/000712

A. CLASSIFICATION OF SUBJECT MATTER INV. C08J5/22 C08F8/20 C08F8/44 B01J41/14 B01D61/00 C02F1/469 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) C08J C08F B01J B01D C02F 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, COMPENDEX, WPI Data								
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category*</th> <th style="width: 70%; padding: 5px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%; padding: 5px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> MICHAEL HIBBS ET AL: "Poly(phenylene)-Based Anion Exchange Membranes for Alkaline Fuel Cells", ECS TRANSACTIONS, 1 January 2009 (2009-01-01), pages 89-97, XP055107909, ISSN: 1938-5862, DOI: 10.1149/1.3253365 abstract page 90, line 8 - line 14 page 90, paragraph 4 - page 91, paragraph 4 Scheme 1; page 92 page 94 - page 95; figure 1; table II ----- -/-- </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	MICHAEL HIBBS ET AL: "Poly(phenylene)-Based Anion Exchange Membranes for Alkaline Fuel Cells", ECS TRANSACTIONS, 1 January 2009 (2009-01-01), pages 89-97, XP055107909, ISSN: 1938-5862, DOI: 10.1149/1.3253365 abstract page 90, line 8 - line 14 page 90, paragraph 4 - page 91, paragraph 4 Scheme 1; page 92 page 94 - page 95; figure 1; table II ----- -/--	1
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A	MICHAEL HIBBS ET AL: "Poly(phenylene)-Based Anion Exchange Membranes for Alkaline Fuel Cells", ECS TRANSACTIONS, 1 January 2009 (2009-01-01), pages 89-97, XP055107909, ISSN: 1938-5862, DOI: 10.1149/1.3253365 abstract page 90, line 8 - line 14 page 90, paragraph 4 - page 91, paragraph 4 Scheme 1; page 92 page 94 - page 95; figure 1; table II ----- -/--	1						
☒ Further documents are listed in the continuation of Box C. ☒ 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 17 March 2014	Date of mailing of the international search report 25/03/2014							
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Costantini, Nicola							

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2013/000712

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No

PCT/IN2013/000712

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