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# Ion-exchange membranes: preparative methods for electrodialysis and fuel cell applications

M.Y. Kariduraganavar\*, R.K. Nagarale, A.A. Kittur, S.S. Kulkarni

*Department of Chemistry and Center of Excellence in Polymer Science, Karnatak University, Dharwad-580 003, India  
Tel. +91 (836) 2215372; Fax +91 (836) 2771275; email: mahadevappak@yahoo.com*

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## Abstract

Ion-exchange membranes have been used in various industrial processes, e.g., in the electrodialytic concentration of seawater to produce edible salt, as a separator for electrolysis, in the desalination of saline water by electrodialysis, in the separation of ionic materials from non-ionic materials by electrodialysis, in the recovery of acid and alkali from waste acid and alkali solution by diffusion dialysis, in the dehydration of water-miscible organic solvent by pervaporation, etc. Thus, various ion-exchange membranes have been developed according to their requirements. At the same time, various functions have been required from the ion-exchange membranes. Therefore, this review comprises various methods for the preparations of ion-exchange membranes used in electrodialysis and fuel cell applications.

**Keywords:** Ion-exchange membranes; Electrodialysis; Inter polymer membranes; Polysulfone; 4-vinylpyridine

## 1. Introduction

Today, separation membranes have become essential materials not only in industries, but also in day-to-day life. Thus, innumerable membranes have been developed for the use in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation separation, electrodialysis and in medical use such as artificial kidney [1]. Among these membranes, ion-exchange membranes are one of the advanced separation membranes. The

basic applications of the ion-exchange membrane process are based on the Donnan membrane equilibrium principle and have been paid attention to solve two important environmental problems: (i) recovery and enrichment of valuable ions, and (ii) removal of undesirable ions from wastewater [2], especially to extract toxic metal ions [3]. Basically, the ion-exchange membranes separate cations from anions and anions from cations, so they should have a high transport number for counterions. Such membranes with high transport number have the potential applications in new fields as

\*Corresponding author.

new functional materials in the separation of ionic materials, mostly used in the solutions containing multi-components, such as electrodialytic concentration of seawater to produce sodium chloride, demineralization of saline water, desalination of cheese whey, demineralization of sugarcane juice, etc. In some cases, specific ions have been used industrially: monovalent in permselective ion-exchange membranes [4–7], proton permselective ion-exchange membranes are important [8,9]. Apart from these applications, several trials have been carried out to be used as sensors such as humidity sensor [10–12], carbon monoxide sensor [13], drug sensor [14], carriers for enzymes [15], solid polyelectrolytes [7], a carrier for functional materials [16], generation of photovoltage and photocurrent [17], etc. The generation of photovoltage from anion exchange membranes is a new phenomenon and might lead to a new application of the ion-exchange membranes.

For these wide applications, the most desired properties required for the successful ion-exchange membranes are: (1) high permselectivity — an ion-exchange membrane should be highly permeable to counter-ion, but should be impermeable to co-ions; (2) low electrical resistance — permeability of an ion-exchange membrane for the counter-ions under the driving force of an electrical potential gradient should be as high as possible; (3) good mechanical stability — membrane should be mechanically strong and should have a low degree of swelling or shrinkage in transition from dilute to concentrated ionic solutions; (4) high chemical stability — membrane should be stable over a wide pH-range from 0 to 14 and in the presence of oxidizing agents.

The parameters determining the above membrane properties often have the opposing effect. For instance, a high degree of crosslinking improves the mechanical strength, but increases the electrical resistance while more ionic charges in the membrane matrix leads to a low electrical resistance, but in general, causes a high degree of swelling combined with poor mechanical stability.

Thus, there is a compromise between these properties to develop good ion-exchange membranes.

In the past, excellent review articles appeared on different aspects of ion-exchange membranes. However, none of the articles was dedicated to compile the different methods for the preparation of ion-exchange membranes. Therefore, in this review a sincere effort has been made to compile and discuss the different preparative methods of ion-exchange membranes used for electrodialysis and fuel cell applications.

## **2. Types of ion-exchange membranes**

Most commercial ion-exchange membranes can be divided, according to their structure and preparation procedure, into two major categories, either homogeneous or heterogeneous. According to Molau [18], depending on the degree of heterogeneity of the ion-exchange membranes, they can be divided into the following types: (a) homogeneous ion-exchange membranes, (b) interpolymer membranes, (c) microheterogeneous graft- and block-polymer membranes, (d) snake-in-the-cage ion-exchange membranes and (e) heterogeneous ion-exchange membranes.

All the intermediate forms are considered as the polymer blends from the viewpoint of macromolecular chemistry. As a consequence of the polymer/polymer incompatibility, on one hand, a phase separation of the different polymers is obtained, while on the other hand, a specific aggregation of the hydrophilic and hydrophobic properties of the electrolyte is obtained. A classification of the membrane morphology is then possible, depending on the type and size of the microphase. The membranes are translucent, an indication that in homogeneities, if any, are smaller than the wavelength of visible light (400 nm). Thus, these membranes are called interpolymer or micro heterogeneous membranes.

### 3. Preparation of ion-exchange membranes

As far as their chemical structure is concerned, ion-exchange membranes are very similar to normal ion-exchange resins. From chemical point of view, these resins would make excellent membranes of high selectivity and low resistivity. The difference between membranes and resins arises largely from the mechanical requirement of the membrane process. Unfortunately, ion-exchange resins are mechanically weak, cation resins tend to be brittle, and anion resins soft. They are dimensionally unstable due to the variation in the amount of water imbibed into the gel under different conditions. Changes in electrolyte concentration, in the ionic form, or in temperature may cause major changes in the water uptake and hence in the volume of the resin. These changes can be tolerated in small spherical beads. But, in large sheets that have been cut to fit an apparatus, they are acceptable. Thus, it is generally not possible to use sheets of material that have been prepared in the same way as a bead resin. However, the most common solution to this problem is the preparation of a membrane with a backing of a stable reinforcing material that gives the necessary strength and dimensional stability.

#### 3.1. Homogeneous ion-exchange membranes

The method of making homogeneous ion-exchange membranes can be summarized in three different categories:

1. Polymerization or polycondensation of monomers; at least one of them must contain a moiety that either is or can be made anionic or cationic groups, respectively.
2. Introduction of anionic or cationic moieties into a preformed solid film.
3. Introduction of anionic or cationic moieties into a polymer, such as polysulfone, followed by dissolving the polymer and casting it onto a film.

##### 3.1.1. Membranes prepared by polymerization and polycondensation of monomers

Under this category, the membranes prepared from polymerization and polycondensation of monomers, in which, at least one of them must contain a moiety that is or can be made anionic or cationic, respectively are discussed. Under the polycondensation type of the membranes, formaldehyde is used as a crosslinking agent to make the membrane water insoluble, while using suitable monomeric/polymeric material endowed with ion-exchange properties. The first membranes made by polycondensation of monomers followed by crosslinking with formaldehyde were prepared from phenolsulfonic acid [19].

In the actual scheme, the phenol was treated with concentrated sulfuric acid at 80°C, which leads to phenolsulfonic acid in para form, a brown, crystalline material. This acid was then reacted with 38% solution of formaldehyde in water initially at –5°C for about 30 min and then at 85°C for several hours. The solution was then cast into a film, which forms a cation-exchange membrane after cooling to room temperature. Excess monomer can be removed by washing the film in the water. With a slight modification of this procedure, condensation of anisole or sulfonated phenol with formaldehyde and subsequent casting of the membrane on glass plate or mercury followed by curing at 90°C gives the cation-exchange membrane [20]. Like wise, anion-exchange membrane has been prepared by condensation of *m*-phenylene diamine or aliphatic diamine compounds such as polyethylenediamine or dicynodiamines with formaldehyde [21]. The resulting membranes showed good electrochemical properties, but lack in mechanical strength. The membranes prepared from dimethyl-2-hydroxy benzyl amine, phenol and formaldehyde [22]; condensation of  $C_6H_4(OH)_2$  or 1,2,3,  $C_6H_3(OH)_3$  and  $NH_2C_6H_4COOH$  with formaldehyde [23]; benzidine-formaldehyde condensate with binder of acrylonitrile-vinylchloride copolymer [24]; and phenolsulfonic acid cross-linked with formaldehyde supported on orlar cloth

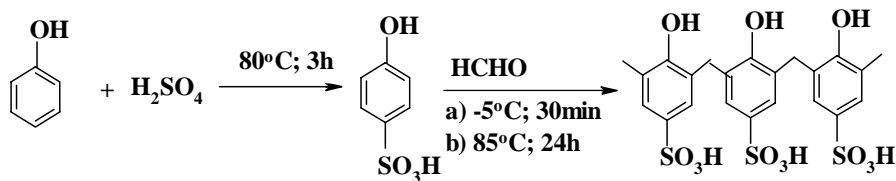


Fig. 1. Reaction of phenol sulfonic acid with formaldehyde.

[25]. The reaction for the above membranes is shown in Fig. 1.

### 3.1.2. Fluorinated ionomer membranes

These membranes are prepared by the polymerization of monomers, which contain a moiety that can be made either cationic or anionic by further treatment. These membranes are mainly developed for the applications in the chlor-alkali industries and for the fuel cell applications [26], since most of the conventional hydrocarbon ion-exchange membranes degrade in the presence of the oxidizing agent, especially at elevated temperatures. These are the fluorocarbon-based ion-exchange membranes (Nafion) with good chemical and thermal stability have been developed by DuPont [27]. There is four-step procedure for the synthesis of Nafion membranes: (a) the reaction of tetrafluoroethylene with  $\text{SO}_3$  to form the sulfone cycle; (b) the condensation of these products with sodium carbonate followed by copolymerization with tetrafluoroethylene to form the insoluble resin; (c) the hydrolysis of this resin to form a perfluorosulfonic polymer, and (d) the chemical exchange of the counter ion,  $\text{Na}^+$  with the proton in an appropriate electrolyte. DuPont introduced this membrane in 1966 following the reaction route shown in Fig. 2. These are high equivalent weight (EW) perfluorinated membranes and have limited their use in fuel cells because they consume high power density.

The Dow Chemical Company has overcome this problem with the development of low EW perfluorinated membranes produced in 1988. The Dow membrane is prepared by the copolymeri-

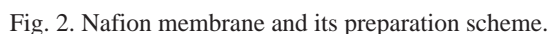
zation of tetrafluoroethylene with vinyl ether monomer as per the reaction scheme shown in Fig. 3.

The polymer can be described as having a Teflon-like backbone structure with a side chain attached via an ether group. This side chain is characterized by a terminal sulfonate functional group. It must be pointed out that the Dow monomer is more complicated to elaborate than the DuPont monomer. The synthesis of Dow epoxy (Fig. 3) is more complicated than that of the Nafion epoxy (Fig. 2) [28], which is a commercially available material [29]. The perfluorinated ionomer membrane has also been developed by the Asahi Glass Company and commercialized as Flemion. The general properties of the long-side-chain perfluorinated ionomer membranes (e.g., Nafion/Flemion/AcipleX) and the short-side-chain perfluorinated ionomer membranes (e.g., Dow) are as follows: (a) EW range = 800–1500; (b) conductivity = 0.20–0.05 S/cm<sup>2</sup>.

## 3.2. Introduction of anionic or cationic moieties into a preformed solid film

### 3.2.1. Styrene-divinylbenzene-based membranes

Styrene-divinylbenzene-based membranes come under this category. Several references are there on the preparation of these membranes [30–34]. These are the best-known membranes in the literature for the application of electrodialysis. Copolymerization of styrene and divinylbenzene, followed by sulfonation and amination in solution or in bulk gives the cation and anion-exchange



membranes, respectively. The cation-exchange membrane was prepared by the sulfonation of polymer with chlorosulfonic acid or with concentrated sulfuric acid in dichloroethane using the silver sulfate as catalyst. The anion-exchange membrane was prepared by chloromethylation of the polymer followed by the amination. The reaction scheme for these membranes is as shown in Fig. 4. It is known [33] that for the pure styrene-divinylbenzene cation-exchange membrane, selectivity for the monovalent ion is poor. It is also known that there is no remarkable effect of crosslinking agent on the selectivity of particular cations. Though the mobility of the multivalent cations decreases with increasing the crosslinking, because of the compact structure of the membrane. From the point of commercial application, special types of ion selective membranes have been prepared using these monomers. Such as membranes for monovalent ion selective for the production of table salt, the membranes for high hydrogen ion retention to recover acids from the waste water, etc. The hydrogen ion can pass selectively through the membrane against all other ions in electrodialysis, so the development of membranes with high acid retention was really a challenging task for the applications of acid recovery. Sata et al. [33–36] had done lot of work on the monovalent ion selective membranes for the application of production of table salt from seawater. They reported the modification of permselectivity between ions with the same charge through ion-exchange membranes in electrodialysis and they have been classified according to its mechanism. The first is the sieving of the ions with changing crosslinkage of the membrane, the second is the effect of charge, electrostatic repulsion and on permselectivity of ions, and the third is the specific interaction between the specific ion-exchange groups, the membrane matrix and the ions. In case of anion-exchange membrane, sieving of ions by highly crosslinked layer was effective on changing the permselectivity between chloride and sulfate ions. Also sieving can be done effectively by

introducing the dense polyelectrolyte layer on the membrane surface, like polymerization of the pyrrole on the surface of the cation and anion-exchange membranes to change the permselectivity of the larger ion, such as calcium and sulfate ion with respect to sodium and chloride ions, respectively.

Selective permeation of specific ions is mainly dependent on the degree of affinity of specific anions with the anion-exchange membrane, and partially on the change in mobility through the membrane. The affinity of the specific ions to the membrane depends on the balance of hydrophilicity of the membrane, as done by introducing the polysoap layer made up of poly(*n*-dodecyl-4-vinylpyridine bromide) on the anion-exchange membrane. Utilization of electrostatic repulsion force to change the permselectivity has been studied from various aspects and this was effective on achieving monovalent cation and monovalent anion permselectivity [34,35]. It is also reported that a bipolar ion exchange membrane is selectively permeate to lower valent cations compared to higher ones.

In a special type of membrane [36], synergistic effect of the change in ion-exchange equilibrium constants of various anions to chloride ions and the change in the ratio of mobility between anions have been studied by developing membranes from poly(vinyl alcohol),  $\beta$ -cyclodextrin and poly(*n*-ethyl-4-vinylpyridinium bromide) by the casting method, followed by crosslinking with formaldehyde. Cyclodextrin is the naturally occurring cyclic oligosaccharides, mostly consisting of six, seven and eight D-glucose units for  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrin, respectively. The doughnut-shaped cyclodextrin has an interior cavity with a diameter of 4.7–5.3 Å ( $\alpha$ -CD), 6.0–6.5 Å ( $\beta$ -CD) or 7.5–8.3 Å ( $\gamma$ -CD) [36]. They have a unique configuration, which makes the outer surface hydrophilic and the inner cavity hydrophobic in nature. Because of the presence of hydrophilic outer surface and hydrophobic inner cavity, it was expected that the permeation of different anions through



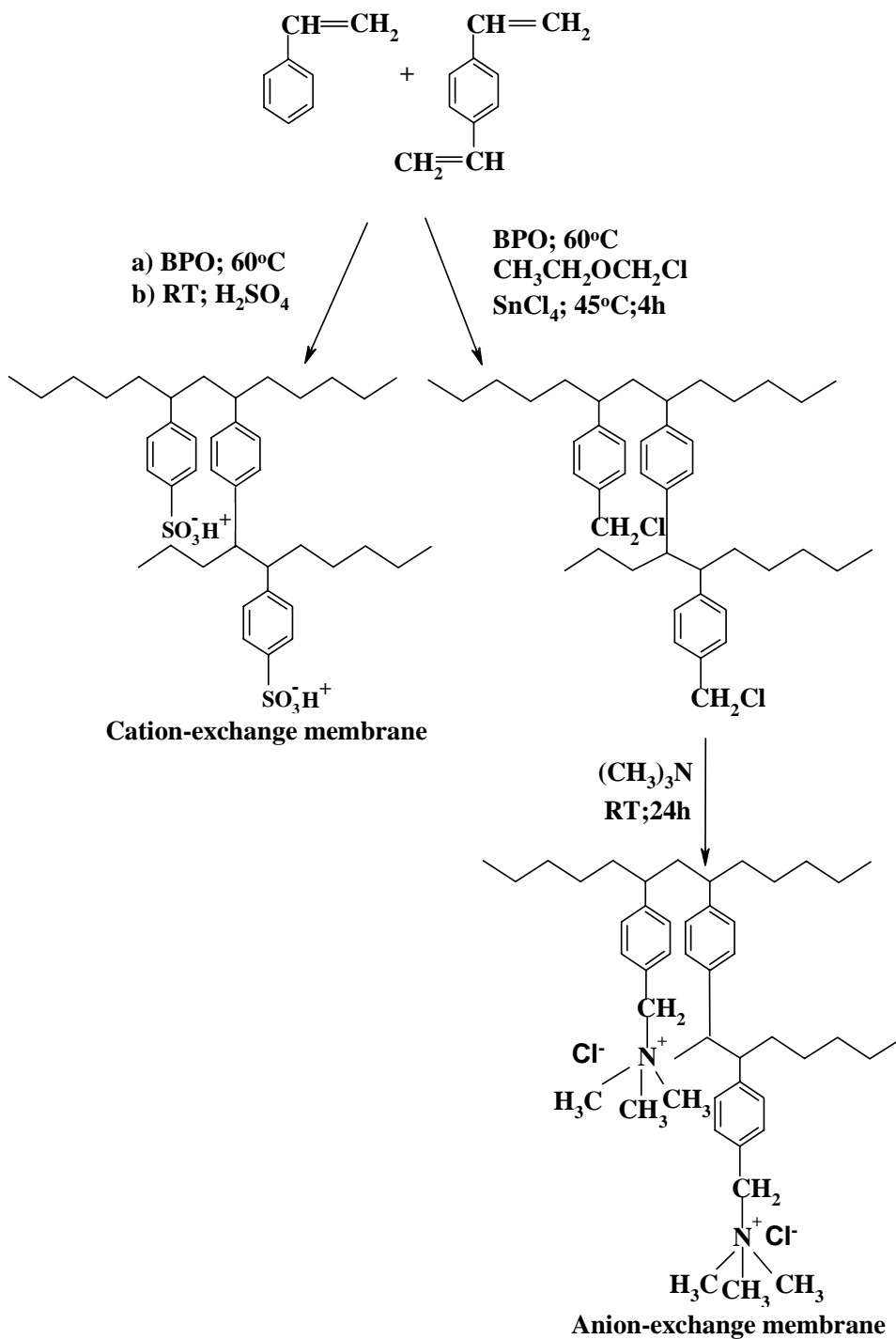


Fig. 4. Reaction scheme for styrene divinylbenzene based ion-exchange membranes.



the anion-exchange membrane would be different. On the other hand, it was reported that the permselectivity of anions through anion-exchange membranes in electrodialysis is mainly governed by a balance of the hydrophilicity of anion-exchange membranes with the hydration energy of anions in permeating through the membrane [36].  $\beta$ -cyclodextrin makes the membrane hydrophilic, in which water content of the membranes increased with increasing the content of  $\beta$ -cyclodextrin. Consequently, transport numbers of the less hydrated anions, nitrate and bromide ions, relative to chloride ions decreased and those of strongly hydrated anions, sulfate and fluoride ions, increase with increasing the content of  $\beta$ -cyclodextrin.

The anion-exchange membrane prepared from the copolymerization of the 4-vinylpyridine and divinylbenzene followed by quaternization with

methyl iodide gives the membrane with good electrochemical properties, but lacks in chemical stability.

Very recently our group [37] has developed the novel homogeneous anion-exchange membranes by polymerisation of 4-vinylpyridine and simultaneously crosslinking with epichlorohydrin and aniline on a oven support cloth at different ratios. The reaction was carried out at 80°C temperature in the presence of benzoyl peroxide as an initiator. The resulting membranes were quaternised with methyl iodide using hexane as a solvent. The scheme of the reaction is shown in Fig. 5.

These membranes exhibited good electrochemical properties and mechanical strength, and can be used for the conversion of sea and brackish water into potable water, production of salt from seawater and also used in chlor-alkali production.

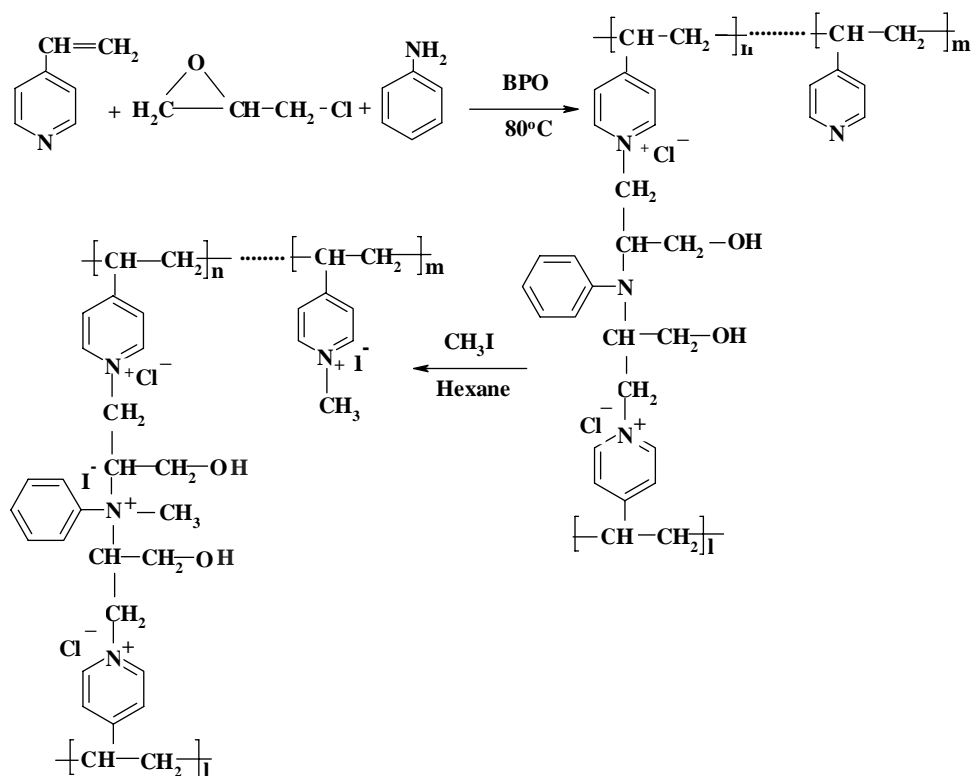


Fig. 5. Poly(4-vinylpyridine) based anion exchange membrane.

### 3.2.2. Partially fluorinated ionomer membranes

The preparation of the monomer  $\alpha,\beta,\beta$ -trifluorostyrene was carried out by Cohen et al. [38], even though the poly- $\alpha,\beta,\beta$ -trifluorostyrene was first synthesized by Prober [39]. The structure of the polymer is shown in Fig. 6. Hodgdon [40] has investigated the sulfonation of  $\alpha,\beta,\beta$ -trifluorostyrene seeking their applications to fuel cells. From optimization of reaction conditions, he has prepared a multiplicity of equivalent weight or different ion-exchange capacity of both linear and crosslinked poly- $\alpha,\beta,\beta$ -trifluorostyrene sulfonic acids. He has shown that the extreme difficulty in sulfonation of poly- $\alpha,\beta,\beta$ -trifluorostyrene was caused by the beta-directing influence of the perfluorinated polyalkyl group attached to the aromatic ring [39]. The degree of sulfonation was very much dependent on the temperature used in sulfonation as well as the concentration of chlorosulphonic acid. The linear poly- $\alpha,\beta,\beta$ -trifluorostyrene sulfonic acid was prepared by a direct combination of chlorosulphonic acid with trifluorostyrene. Sulfone crosslinked poly- $\alpha,\beta,\beta$ -trifluorostyrene sulfonic acid was prepared and was found to be totally resistant to oxidative mode of degradation, which causes drastic oxidative depolymerization of polystyrene and polystyrene-divinylbenzene sulfonic acids. This is attributed to the substitution of fluorine in place of benzyl-

hydrogen atom of polystyrene leading to the added C–F bond strength required to resist the oxidation environment. Thus, it was claimed that the high stability of fluorine atoms attached to alkyl carbon atoms impacts the oxidative and thermal stability superior to that exhibited by the conventional ion-exchange polymers such as styrene sulfonic acid.

### 3.3. Introduction of anionic or cationic moieties into the polymer

#### 3.3.1. Polysulfone-based ion-exchange membranes

For the purpose of applying electrodialysis process under severe conditions such as high temperature and strongly oxidizing conditions, a more stable Nafion and Dow ion exchange membranes have been developed and successfully applied under those conditions. It was found that only a few major industrial applications were sought other than the chlor-alkali industry, primarily because of its high cost. Thus, there has been a challenge to develop new types of ion-exchange membranes, which would be cheap but also have good electrochemical properties and excellent resistance to degradation by heat and chemical attack.

Engineering plastics such as polysulfone and polyethersulfone have been widely used as a base polymer for ultrafiltration and gas separation because of their excellent workability and mechanical

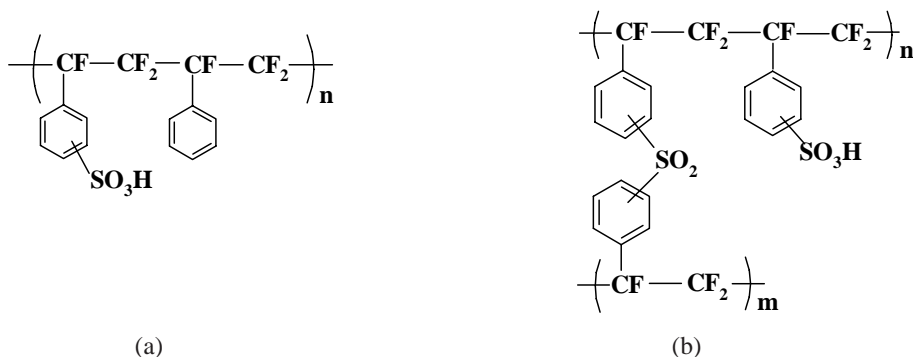


Fig. 6. Poly(trifluorostyrene) based ion-exchange membranes: a) linear; b) crosslinked.

strength [41–44]. In particular, a polysulfone membrane having excellent chemical resistance has been studied for its application as an ion-exchange membrane by improving the permeability for ultrafiltration and reverse osmosis or imparting ion permselectivity by introducing the ion-exchange groups into the membrane [45–47]. Several researchers [48–50] have prepared the ion-exchange membranes using polysulfone as a base polymer of the membrane. The sulfonation procedure was achieved either by the solution procedure [51] or by the slurry procedure [52] and their properties have been described [49,53,54]. The sulfonation procedures for poly(arylene ether sulfone) Udel P-1700 (PSU) and Vitrex PES 5200P (PES) described in the patent literature [52].

A new sulfonation process for polysulfone ionomers has been proposed [49,55–59]. It was reported that these polymers have been cross-linked into membranes by a new crosslinking procedure. The basic working hypothesis for the new type of sulfonation method was that poly(sulfone) Udel as shown in Fig. 7 is usually sulfonated at the ortho position to the ether bridge of the bis-phenol-A-position by electrophilic substitution [60], because this part of the molecule has high electron density in contrast to the diarylsulfone portion of the repeating monomer unit, which has a low electron-density due to the electron-withdrawing  $\text{SO}_2$  group. One disadvantage of electrophilically sulfonated poly(sulfone) is that the  $\text{SO}_3\text{H}$  group at this position can undergo ipso-substitution with  $\text{H}^+$ , which lowers the hydrolytic stability of the sulfonated poly(sulfone) in strong acids. This limits the application of the commonly sulfonated poly(sulfone) as a cation-exchange

polymer in electro-membrane process. Thus, the new method is based on the sulfonated polysulfone in the diarylsulfone part should show increased hydrolytic stability against ipso-substitution by  $\text{H}^+$  compared to electrophilically sulfonated polysulfone, due to the electron-deficient of the diarylsulfone position of the polymer.

Based on the literature [59], it was found that polysulfone Udel can be substituted in the electron deficient portion of the monomer by first deprotonating the aromatic ring position ortho to the sulfone bridge with metalorganic reagents and subsequent reaction of the metalated site with the electrophiles. Deprotonation reactions by attack of metalorganics at the polymer backbones are also known from poly(2,6-dimethyl-para-phenylene ether) (PPO), poly(styrene), poly(vinylthiophene) and poly(methylphenylphosphazene). To convert the metalated site of the deprotonated polymer into sulfonic acid group, the metalated polymer is quenched with the electrophile  $\text{SO}_2$ , and the metal sulfinic acid derivative of the respective polymer is formed. Sulfinates and particularly, the corresponding sulfinic acids are known to be chemically unstable and can easily be oxidized to sulfonic acids.

Based on the aforementioned facts, a three-stage process has been developed for introduction of sulfonic acid group in diarylsulfone part of the poly(sulfone) Udel. The scheme for this process is presented in Fig. 8. The sulfonation process consists of the following steps: (a) lithiation of the polymer in a 2.4 wt % THF solution with 10 N *n*-butyl lithium, at temperature ranging from  $-50$  to  $-80^\circ\text{C}$  under argon condition. The lithiation proceeds very fast (0.5 h) and is nearly quantitative, as has been proved by NMR; (b) introduction of  $\text{SO}_2$  into the reaction vessel containing the lithiated polymer at temperature from  $-65$  to  $-20^\circ\text{C}$ . The reaction of the lithiated polymer with the electrophile,  $\text{SO}_2$  is also nearly quantitative as has been proved by NMR. The sulfonation reaction is finished after 5–10 min of  $\text{SO}_2$  introduction; (c) oxidation of the formed sulfinic acid. Alkaline or

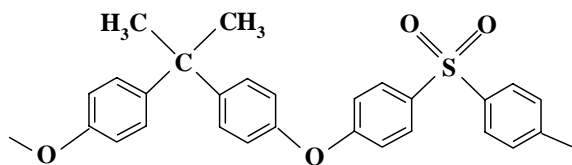


Fig. 7. Structure of Udel polysulfone.

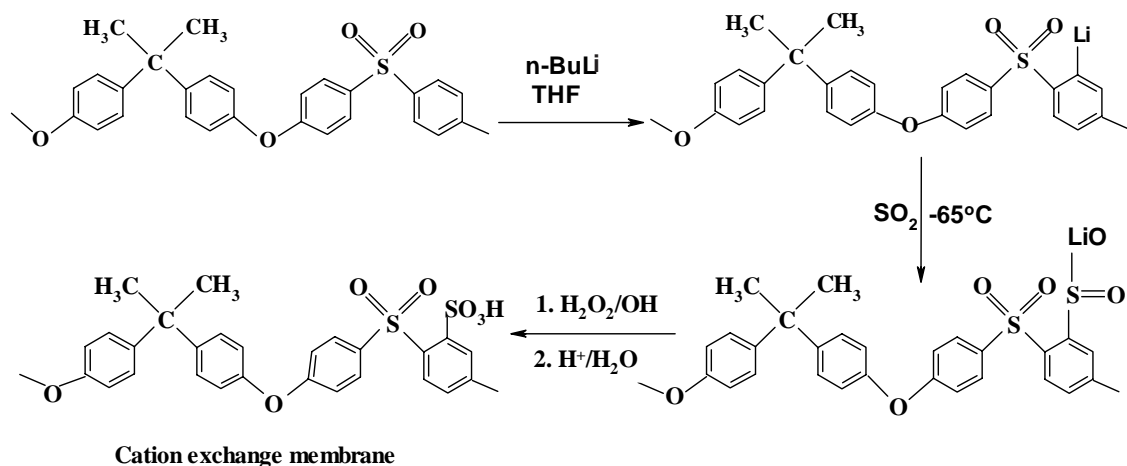


Fig. 8. Schematic presentation of sulfonation of Udel polysulfone membrane.

neutral  $\text{H}_2\text{O}_2$ , sodiumhypochloride, or  $\text{KMnO}_4$  solution has achieved the oxidation with aqueous solution or suspension after isolating the polymeric sulfinate; and (d) conversion of lithium sulfonate to the corresponding sulfonic acid by aqueous  $\text{HCl}$  (water insoluble polymeric sulfonic acids) or by stirring of the sulfonate with a cation-exchange resin (water-soluble polymeric sulfonic acid).

The ion-exchange capacity (IEC) of the resulting polymer is largely dependent upon the oxidation step. A loss in sulfinate groups can partially be caused by splitting-off of the sulfinate group during the oxidation process and subsequent substitution by hydrogen (ipso reaction). However, by selecting the suitable oxidation conditions the loss in IEC can be minimized, as can be seen at the oxidation of poly(sulfone)- $\text{SO}_2$ -25 with  $\text{KMnO}_4$ , where 98.9% yield of the oxidation products are obtained. At higher to medium degree of sulfination,  $\text{KMnO}_4$  and  $\text{NaOCl}$  are the most suitable oxidants (3.3–1.9 mequiv/g of IEC). For the low degree of sulfination, nonionic oxidant  $\text{H}_2\text{O}_2$  should be used. The membrane swelling largely depends upon the IEC. At IECs of  $\geq 2.4$  mequiv  $\text{SO}_3\text{H/g}$  dry polymer, the polymer becomes water-soluble. The specific conductances

of the membranes dependent upon the IEC and are lower than the Nafion membrane. This can be explained by stronger clustering of  $\text{SO}_3\text{H}$  in Nafion due to its extremely hydrophobic backbone [60].

It is reported that [49,61,62] the ion-exchange membranes prepared using polysulfone as a base polymer are likely to undergo a dimensional change during flocculation and tend to have defects. As the ion-exchange capacity (IEC) increases, the affinity towards water molecules increases, whereby it tends to hardly flocculate. Hence, it appears difficult to obtain a membrane having sufficient mechanical strength, since dimensional stability tends to be poor [50]. The water tends to concentrate as molecular clusters around the ionic groups and therefore, the affinity of the membrane towards water molecules increases with IEC. The high affinity towards water leads to low cohesive forces and thereby membrane swells quite strongly in water [61].

Terada et al. [51,63] have reported a new type of ion-exchange membrane. Their study demonstrated that an ion-exchange membrane formed by using a block copolymer having segments, to which ion-exchange groups can be introduced readily, had a higher mechanical strength as

compared with the type of ion-exchange membranes formed by segments, to which ion-exchange groups can hardly be introduced. The advantage of the block copolymer is that the cohesive force of the part of polymer without ionic groups controls the membrane swelling. The anion-exchange membranes have been prepared by block copolymers of polysulfone and polyphenylenesulfidesulfone in two steps: In the first step chloromethylation of the polymer and in the second step, amination of chloromethylated copolymers [61]. These membranes have shown good dimensional stability with poor electrochemical properties. Sulfonation of the copolymer with triethylphosphate and sulfuric acid yields cation-exchange membranes with poor electrochemical properties [64].

### 3.3.2. Partially sulfonated polyether ether ketone membranes

The electrophilic aromatic sulfonation of the polyether ether ketone (PEEK) was established in the literature [65]. The general concept of the sulfonation consists in dissolving the dried PEEK in concentrated sulfuric acid. The desired level of sulfonation depends on the time and temperature of the process. For instance, Bailey et al. [66] have sulfonated the PEEK by dissolving 10 g of the oven dried PEEK in 100 ml of 96%  $\text{H}_2\text{SO}_4$ . The time and temperature of the deep red viscous solution were varied in order to achieve the desired level of sulfonation. The reaction was quenched by slowly pouring the acidic solution into one liter of distilled water. The precipitation of the polymer may appear instantly forming a continuous string. In the last step, the polymer was extensively washed to remove the excess acid and dried in a vacuum oven at 100°C [66].

Unfortunately, these membranes have swollen in a gel-like state, making them mechanically fragile. Because of this behaviour, the lifetime of the membrane in electrolysis system can be limited. There are different strategies for the reduction of swelling of the ion-exchange membranes.

They are: crosslinking the polymer with suitable crosslinking agent, blending the polymer, which are capable of formation of hydrogen bonds. The formation of hydrogen bonds leads to compatibilization of the blend polymers. Many examples of this type of blend are mentioned in the literature [67]. Kerees et al. [68] developed the ion-exchange membranes by blending of sulfonated poly(ether ether ketone) with the aminated polysulfone Udel ( $\text{PSU-NH}_2$ ), polyamide, PA 6-3-T (Trogamid P) (Huls) and poly(etherimine) PEI Ultem (General Electrical). In the blend membrane, swelling was reduced by specific interaction in case of blend components PA and PEI hydrogen bonds, and in the case of the blend component  $\text{PSU-NH}_2$  (partial) polysalt formation, leading to electrostatic interaction between the blend component macromolecules and hydrogen bonds.

The acid-base interactions also led to a decrease of ionic conductivity by partial blocking of  $\text{SO}_3^-$  groups for cation transport, when compared with the ionic conductivity of the hydrogen bond containing blends. The acid-base blends showed better ion permselectivities than the hydrogen bond containing blends, even at high electrolyte concentrations, and thus, they have a better performance in electrodialysis. The thermal stability of the blends is good and in case of acid-base blend it is still better. The investigated blend membranes showed similar performance as the commercial cation-exchange membrane CMX in electrodialysis (ED) application. The performance of the acid-base blend membrane is better than the performance of the hydrogen-bonded PEEK-PA blend, especially in ED experiment applying the higher NaCl concentration. This may be due to lower swelling and thus, better ion permselectivity of the acid-base blend membranes, when compared to the PEEK-PA blend.

### 3.3.3. Polyphosphazene ion-exchange membranes

Polyphosphazenes are the new class of base-

polymers for ion-exchange membranes because of their reported thermal and chemical stability, and the ease of chemically altering the polymer by adding various side chains onto the  $\text{--P=N--}$  backbone. Sulfonated polyphosphazene cation-exchange membranes are an attractive alternative to perfluorosulfonic acid and polystyrene sulfonate membranes. However, there are few reports in the literature on the fabrication and properties of ion-exchange membranes from the sulfonated polyphosphazenes. The difficulty associated with producing such membranes lies in preparing the sulfonated polyphosphazene and, more importantly, in balancing the hydrophilicity of the resulting polymer to prevent dissolution in aqueous solution [69].

One of the main methods for the synthesis of these polymers is illustrated in Fig. 9.

Poly(dichlorophosphazene) reacts with a wide variety of nucleophiles to yield high molecular weight organic-derivatized polymers with properties that vary widely with the side group structure. The stability of the phosphorus-nitrogen backbone makes this class of macromolecules particularly suitable for side-group and surface modification. Allcock et al. [70] reported that the molecular level and surface sulfonation of aryloxy- and arylamino phosphazene was accomplished through the use

of concentrated sulfuric acid. Allcock et al. also reported [71] that sulfonation of aminophosphazene with 1,3-propanesulfone, but the yield was very low. Montoneri, et al. [72,73] shown that aryloxy polyphosphazene can also be sulfonated via the use of sulfur trioxide. The sulfonation of poly[bis(phenoxy)phosphazene] in dichloromethane with  $\text{SO}_3$ , it was found that when the mole ratio of  $\text{SO}_3$  to phosphazene was less than one, there was no C-sulfonation and up to 50% of the skeleton nitrogens were attacked to form  $\equiv\text{N}\rightarrow\text{SO}_3$  complex. For  $\text{SO}_3$ /polyphosphazene molar ratios greater than one, C-sulphonation was observed, mainly at the meta-position in the phenoxy side groups.

Usually, sulfonation of polyphosphazene yields water-soluble polymers [69]. So, in practice, water insoluble sulfonic acid membranes from polyphosphazene polymers can be made which involve the crosslinking polyphosphazene membranes followed heterogeneous sulfonation [73]. Alternatively, homogeneous or heterogeneous polymer sulfonation is carried out, followed by film casting and crosslinking. These two methods require that the polyphosphazene contains side groups that can be used for crosslinking or in the second case, sulfonate groups can serve this purpose [74]. The water insoluble polyphosphazene can be made by

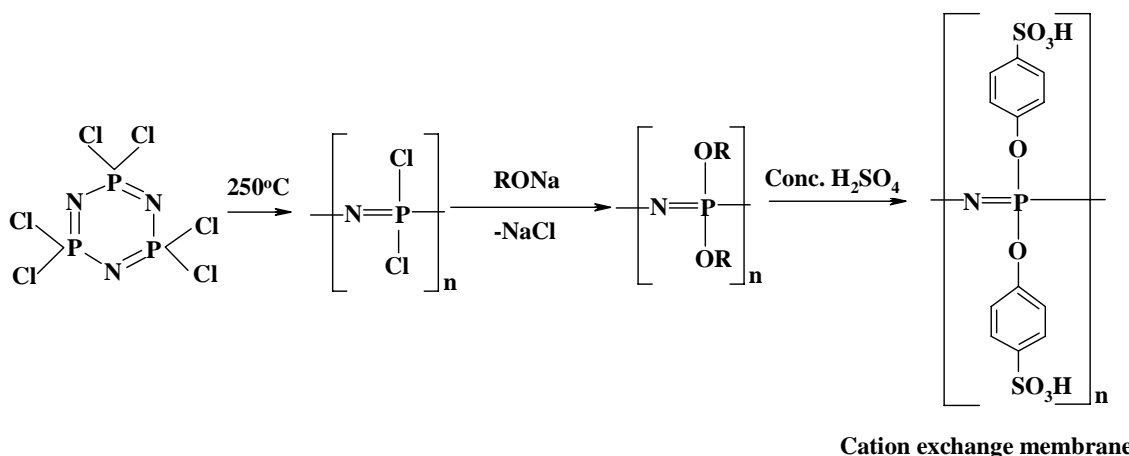


Fig. 9. Reaction scheme for sulfonation of poly(phosphazene) membrane.



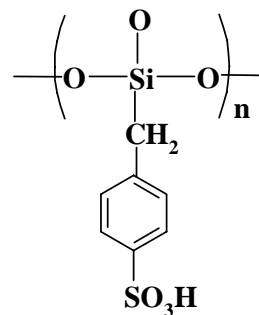
introducing the alkyl groups on the phenoxy ring followed by controlling mole ratio of sulphonating agent to polyphosphazene mole ratios [75].

### 3.4. Styrene/ethylene-butadiene/styrene triblock copolymers

Styrene/ethylene-butadiene/styrene triblock polymer is a commercially available product (Kraton G1650) containing a saturated carbon center block, which should be inert to the sulphonation reaction. This polymer has good mechanical and chemical stability [76–78]. The typical casting solvent of the sulphonation process can be reached in *n*-propanol, which should preferentially solvate the sulfonated styrene blocks. It has been claimed that membranes with reproducible properties at a constant sulphonation were obtained. It was also indicated that the conductivities at sulphonation levels above 50 mol% of styrene units exceed that of Nafion under similar measurement conditions. In particular, a sulphonation level of 60% was found to be good balance of electrical and mechanical properties.

#### 3.4.1. Poly(benzylsulfonic acid)siloxane (PBSS)-based membrane

The synthesis of this membrane was obtained by sol-gel process with different steps. It was based on the hydrolysis condensation of the benzyl-triethoxysilane precursor in a methanol solution containing water and triflic acid ( $\text{F}_3\text{SO}_3\text{H}$ ). The steps of preparation are indicated elsewhere [79] and their structure is as shown in Fig. 10. The polymer was sulphonated in dichloromethane solvent using chlorosulfonic acid. Several copolymer compositions prepared from different proportions of the mixture of benzyl-triethoxysilane, *n*-hexyltrimethoxysilane and ethoxysilane (e.g. different organically modified alkoxy silanes). Crosslinking was also performed in THF by hydrosilylation of silane groups with divinylbenzene using divinyltetramethyldisiloxane platinum complex as catalyst. These membranes are



**Cation-exchange membrane**

Fig. 10. Structure of poly(benzylsulfonic acid) siloxane-based membrane.

thermally stable up to 250°C and have shown conductivity of  $1.6 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$  at room temperature [79].

### 3.5. Snake-in-the-cage ion-exchange membranes [80]

Snake-in-the-cage ion-exchange (retardion) membranes can be synthesized by saturation of a suitable ion-exchange resin (the cage) with an organic counter ion that can be polymerized to form a linear chain of oppositely charged polymer (the snake). The polymer chain cannot be removed from the host resin due to strong electrostatic interaction and the restricted mobility of the linear polymer chains. The ionic sites of the resin cage are neutralized in the presence of oppositely charged polymer chains. This provides mechanical stability leading to decreased swelling and shrinking properties.

The main retardion resins are a low affinity for non-electrolyte, coupled with an ability to selectively retard ionic substances. They can therefore be used not only for salting non-ionic solutions, but also for separating unwanted ions from ionic substances. In addition to retention of ions, retardion resins absorb acids and can be used for such purposes as removing excess acid following acid hydrolysis of proteins. The relative mobility of snake polymer chains provides the possibility



of very close contact between oppositely charged groups on retardion resins and is a prime reason for the characteristics of these materials.

### 3.6. Heterogeneous ion-exchange membranes

Ion-exchange membranes, both the homogeneous and heterogeneous, being unique in their nature overcome each other in one way or another. Homogeneous membranes having good electrochemical properties lack in their mechanical strength, whereas heterogeneous membranes having very good mechanical strength are comparatively poor in their electrochemical performance [81]. However, by choosing a suitable binder to make non-reinforced membranes or by choosing a suitable reinforcing fabric, it is possible to have good ion-exchange membranes by an optimum combination of electrochemical properties and mechanical strength with heterogeneous method.

Heterogeneous ion-exchange membranes can be made [82] by mechanical incorporation of powdered ion-exchange resin into sheets of rubber, PVC, acrylonitrile copolymers or some other extrudable or mouldable matrix. Such membranes can be prepared [83] either by (i) calendaring ion-exchange particles into an inert plastic film or (ii) dry moulding of inert film forming polymers and ion-exchange particles and then milling the mould stock or (iii) resin particles can be dispersed in a solution containing a film forming binder and then the solvent is evaporated to give ion-exchange membrane. Such heterogeneous membranes may also be reinforced with a chemically resistance fabric [84].

Kariduraganavar et al. [85] and Adhikari et al. [86,87] found that the particle size distribution of the resin particles of different mesh has been affected the electrochemical and mechanical properties of the membranes. It is observed that with increase in resin loading the membranes become more and more brittle and at the same time it is also observed that the finer the resin particles are, the more flexible is the membrane. For PVC

binder, with resin particles of –300+400 mesh (39  $\mu\text{m}$ ), it is possible to obtain flexible membranes up to 60% resin loading whereas the membranes become brittle even with 40% loading for –100+200 mesh sized (80  $\mu\text{m}$ ) resin particles. The brittleness of the membrane may be due to increased resin loading, which increases after a certain point when phase inversion takes place. The cross-linked resin particles tend to form the continuous phase and binders become the discrete phase. Actually resin particles being the more brittle in nature compare to binder, they fail to acts as impact modifier and crack propagation becomes facile, resulting in a brittle membrane. At any particular blend ratio the finer the resin particles, the more homogeneous the blend is, resulting in a more flexible membrane. As the resin loading increases, the burst strength of the membranes decreases. This may be due to the formation of the continuous phase by the resin particles, which has a lesser impact on the strength. However, the burst strength can be improved by decreasing the particle size.

For practical applications, the dimensional stability in different ionic forms is the most desirable criteria for any commercially successful ion-exchange membrane. The heterogeneous ion-exchange membranes show the good dimensional stability compare to the homogeneous membranes. This may be due to the absence of micro voids in the homogeneous ion-exchange membranes, since, it forms the continuous phase during the polymerization. In case of heterogeneous membranes, the loss of solvent due to evaporation introduces micro voids between the resin particles and binder regions. These micro voids are sufficient to accommodate solvent molecules for the solvation of ionic species in the resin, so the solvation does not manifest the dimensional changes of the membranes. The particle size of the resin also affects the ion-exchange capacity and areal resistance of the membrane. At a definite resin loading and thickness of the membrane, the electrical resistance decreases and ion-exchange

capacity increases with decreasing the particle size. Decreasing the particle size results in the higher surface area of the resin particles. With increase in surface area, the number of functional groups which may actively participate in the transport of counter ions through the membrane results to lower the resistance and higher the ion-exchange capacity of the membranes.

### 3.7. Interpolymer ion-exchange membranes

The interpolymer ion-exchange membranes developed in the literature [86–88] possess an excellent combination of both electrochemical and mechanical properties. For the preparation of interpolymer membrane, linear polyethylene was used as a binder. It was made into an organosol with suitable solvating monomers like styrene-divinylbenzene. This blend, on polymerization of monomers under a free radical mechanism yields a chemical polyblend of two interpenetrating networks of linear and crosslinked polymer molecules [87,88]. In addition, due to grafting there may be an inter crosslinking between polyethylene and polystyrene phase. Such a chemical polyblend behaves like a homogeneous type having less probability of micro voids compare to heterogeneous type membranes. For lack of such available space, when there is solvation of ionic groups, there is an expansion of matrix with the dimensional changes.

Recently [89] ion-exchange membranes, by the semi-interpenetrating polymer networks (s-IPNs) have been prepared by mixing of two polymers such as PVA and polyelectrolytes, followed by gaseous crosslinking with dibromoethane. The polyelectrolytes used to develop tailor-made ion-exchange membranes are, poly(sodium styrenesulfonate) (PSSNa), poly(styrenesulfonic acid) (PSSH) and poly(acrylic acid) (PAA) for cation-exchange membranes and polyethyleneimine (PEI), poly(diallyldimethylammonium chloride) (PDDMACl) and poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDPCl) for anion-exchange membranes. It was found that, for

the 60/40 poly(vinyl alcohol) to polyelectrolyte mass ratio, the homogeneous film with suitable mechanical property was obtained. The membranes PVA/PAA show less ion-exchange capacity and swelling compared to the PVA/PSSNa and PVA/PSSH membranes. The anion-exchange membranes prepared using the above polyelectrolytes are weak ion-exchange membranes.

### 3.8. Membranes prepared by the grafting method

Radiation grafting of polymers is a well-known technique for modification of the physical and chemical properties of the polymer [90–95]. Irradiation of polymers by means of ionizing radiation such as  $\gamma$ -rays induces the formation of radicals on the polymers, polymer main chain from which polymerization of another monomer can be initiated. Therefore, this technique makes it possible to bring together two highly incompatible polymers in one material having combined properties. In recent years, the amount of efforts devoted to use this technique for preparation of various types of membranes significantly increased, because it provides the ability to closely control the membrane composition and properties by proper selection of the degree of grafting. Moreover, it overcomes the membrane shaping problem where grafting can be started with a film already in a membrane form. The ion-exchange membranes made using polyethylene sheets by the grafting method followed by sulfochlorination and amination have exhibited low electrical resistance combined with high permselectivity and excellent mechanical strength. The reaction scheme for the preparation of these membranes is as shown in Fig. 11.

A large number of papers published on radiation grafting of monomers onto polymers films to obtain ionomers for versatile applications, they are used as a anion and cation exchange membranes in electrodialysis processes, water desalination, carrier for immobilization of medical products, separators in alkaline batteries, etc.

Nasef et al. [94] prepared the proton exchange

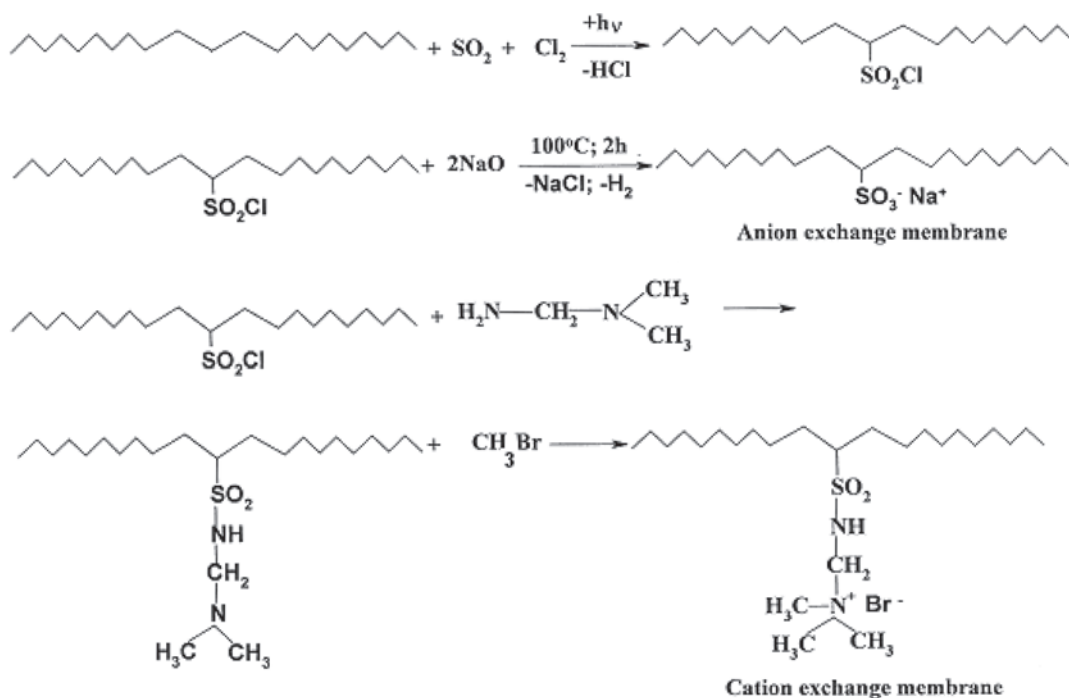


Fig. 11. Schematic presentation of grafting of polyethylene membrane.

membrane by simultaneous irradiation of  $\gamma$ -rays from a  $^{60}\text{Co}$  source at a dose rate of 1.32–15 kGy/h for styrene grafting onto tetrafluoroethylene-co-hexafluoropropylene films at room temperature and sulfonic acid cation-exchange membranes by radiation grafting of styrene onto poly (tetrafluoroethylene-co-perfluorovinyl ether) films followed by a sulphonation reaction. The content of the polystyrene in the membrane was found to be strongly dependent upon the grafting conditions i.e. nature of solvent, dose rate, irradiation time, monomer concentration, etc. Similar behavior was also obtained upon grafting of other monomers such as acrylic acid onto poly(ethylene terephthalate) (PET) films and for grafting of styrene onto normal PET films by pre-irradiation. It was found that the grafted PET films possess good mechanical stability, suggesting their use for the preparation of proton exchange membranes.

Kostov et al. [90–92] showed that the similar

effect of irradiation dose on the anion-exchange membrane prepared by grafting of 4-vinylpyridine (4-VP) onto low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) films by irradiation from  $^{60}\text{Co}$   $\gamma$ -source or high-energy electron beam. The initial properties of the polymer i.e., mechanical strength, thermal and chemical resistance combines with ion-exchange properties of grafted polymer gives valuable properties of the polymer. By varying the reaction conditions of the radiation copolymerisation, grafted copolymers were obtained with degree of grafting from 17.1 to 74.5% for LDPE and from 0.7 to 13.4 for PTFE. The method of multiple grafting was used, involving postpolymerisation effect, which provides possibility for the monomer to penetrate into the polymer matrix together with the stepwise generation of free radicals. It is observed that the linear dependence of the irradiation dose on grafting degree was noticed for both the films.

Irradiation exerts stronger effect on the grafting onto PTFE compared to LDPE, which is connected with the lower radiation resistance of C-F compared with C-H bonds. The water content of the membrane increases linearly with the grafting degree of 4-VP. The thickness of the grafted layer of the 4-VP affects the value of the specific resistances, which decreases with increase in the amount of grafted 4-VP. The membranes exhibit maximum transport number and it varies between 5 and 25% degree of grafting.

#### 4. Conclusion

Although ion-exchange membranes are broadly classified into homogeneous and heterogeneous, but depending on the degree of heterogeneity, these are divided into homogeneous ion-exchange membranes, interpolymer membranes, microheterogeneous graft- and block-polymer membranes, snake-in-the-cage ion-exchange membranes and heterogeneous ion-exchange membranes. The homogeneous membranes prepared by condensation of monomers followed by formaldehyde crosslinking, showed good electrochemical properties, but lack in mechanical strength. However, fluorocarbon based ion-exchange membranes exhibited good electrochemical and thermal stability. These membranes are mainly developed for the chlor-alkali and fuel cell applications, since these are non-degradable in the presence of oxidizing agent at elevated temperatures. High equivalent weight perfluorinated membranes limit their use in fuel cell applications as they consume high power density. This has overcome by the Dow Chemical Company with the development of low equivalent weight perfluorinated membranes.

Styrene-divinylbenzene based membranes have been classified according to its mechanism. The first is the sieving of ions with changing crosslinkage of the membranes, the second is the effect of charge and electrostatic repulsion on perm-

selectivity of ions, and the third is the specific interaction between the specific ion-exchange groups, the membrane matrix and the ions. These membranes exhibit good electrochemical properties, but lack in chemical stability. It was claimed that the high stability of fluorine atoms attached to alkyl carbon atoms impacts the oxidative and thermal stability superior to that exhibited by the conventional ion-exchange membranes. On the other hand, ion-exchange membranes prepared using polysulfone as a base polymer are likely to undergo a dimensional change during flocculation and tend to have defects. Therefore, it is difficult to get membranes with sufficient mechanical strength, since water tends to concentrate as molecular clusters around the ionic groups. However, membranes prepared by block copolymers of polysulfone and polyphenylenesulfidesulfone have shown good dimensional stability with poor electrochemical properties.

Sulfonated polyphosphazene cation-exchange membranes are an attractive alternative to perfluorosulfonic acid and polystyrene sulfonate membranes, but due to difficulty associated in preparation of such membranes and balancing the hydrophilicity restricts this limitation. Heterogeneous membranes are known for good mechanical strength, but poor in their electrochemical performances. It is possible to have good ion-exchange membranes by optimizing the electrochemical properties and mechanical strength with heterogeneous method. On the whole, the heterogeneous membranes show the good dimensional stability compare to homogeneous ion-exchange membranes.

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