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A safer route for preparation of anion exchange membrane from inter-polymer film and performance evaluation in electrodialytic application

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ABSTRACT

The present article describes a greener route to inter-polymer anion exchange membranes (AEMs) utilizing *p*-methylstyrene-co-divinylbenzene (*p*-MS-co-DVB) in place of styrene-co-divinylbenzene (Sty-co-DVB). Polyvinyl chloride (PVC) and polyethylene (PE) were used as binders and films were prepared from the inter-polymers by solution casting and melt extrusion processes, respectively. Functionalization of the films was effected through benzylic mono-bromination followed by quaternization with trimethylamine. This alternative procedure dispensed with the use of chloromethyl ether (CME) which was required for functionalization of styrene-co-DVB-based polymer films. CME is a carcinogen that is hazardous to health. The AEMs were characterized by Fourier transform infrared spectroscopy, solid-state ^{13}C-nuclear magnetic resonance and scanning electron microscopy, as well as by measurements of ion-exchange capacity, water uptake, mechanical properties (stress–strain curve), and electrical properties such as ionic resistance and transport number. The *p*-MS-co-DVB/PE AEM, exhibited high transport number (0.95 by the EMF method; NaCl electrolyte) and the electrodialytic desalination efficiency exceeded that of the Sty-co-DVB/PE interpolymer AEM prepared previously. It also exhibited excellent mechanical strength and stability.

1. Introduction

Ion exchange membranes (IEMs) find applications in fuel cells, batteries, chlor-alkali manufacture, electrodialysis and numerous other important commercial processes [1–5]. Demand for IEMs will rise rapidly in the coming years with greater emphasis on desalination, cleaner technologies and emerging applications such as salinity gradient energy [6,7], and alkaline fuel cell technology [8]. Polystyrene-co-divinylbenzene (pSty-co-DVB) polymeric films have been popular for the cost-effective preparation of both cation exchange membranes (CEM) and anion exchange membranes (AEM). The former are readily obtained through sulfonation of the aromatic ring with chlorosulfonic acid whereas the latter are prepared through halomethylation, especially chloromethylation, followed by quaternization [9–11]. Several types of polymers have been employed in AEM preparation, for example, polystyrene [9–11], polysulfone [12], polyether imide [13], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [14], poly(arylene ether) [15], poly(phthalazinone ether ketone) (PPEK) [16], and poly(phthalazinone ether sulfone ketone) (PPESK) [17]. These have been subjected to chloromethylation and thereafter modified suitably for diverse membrane applications such as in fuel cells [18], biomedical devices [19,20], pervaporation [21], solid state polypeptide synthesis [22], etc.

Chloromethyl ether (CME) was used traditionally for chloromethylation reaction. CME, unfortunately, is carcinogenic and hazardous and its use has been restricted since 1970s [23]. Alternative methods have been proposed to minimize the hazards involved in the preparation of AEMs such as in-situ generation and use of CME to eliminate its handling [24], chlorination of vinyl aromatic polymers using sulfuryl chloride [25], and polymerization of halomethyl substituted aromatic monomers, such as chloromethylstyrene [26]. The monomer is expensive, however, and increases the manufacturing cost of membrane. Another difficulty is that it can cause irritation and burning sensation and is therefore best avoided.

Benzylic bromination of polymers is an alternative, simple and promising method for preparation of AEMs, as this approach too provides access to quaternary ammonium moieties. Polymers such as polysulfone [27,28], PPO [29,30], poly(phenylene) [31], and poly (arylene ether ketone) [32], have been utilized to obtain AEMs via bromination and subsequent quaternization. These membranes have high IEC, high ionic conductivity, low water uptake, and are generally employed in fuel cell applications. This approach has,

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however, not been exploited in the preparation of interpolymer AEMs which have excellent durability and are suitable for diverse applications [33,34]. The present work focuses on such AEM preparation, replacing styrene with *p*-methylstyrene (*p*-MS). Specifically, inter-polymer films of *p*-MS-co-DVB/PVC and *p*-MS-co-DVB/PE were prepared through solution casting and melt extrusion processes, respectively, and subjected to benzylic bromination followed by amination to obtain quaternary ammonium sites. The prepared AEMs were characterized physico-chemically and their performances were also evaluated in electrodialysis.

2. Experimental

2.1. Materials

Para methylstyrene (*p*-MS 96%) and divinyl benzene (DVB 80%) were purchased from Sigma-Aldrich Chemicals and used after purification. Benzoyl peroxide (BPO 98%) (SD Fine-Chem Ltd., India) was re-crystallized from chloroform prior to use. Tetrahydrofuran (THF), carbon tetrachloride (CCl_4), dichloroethane (DCE), xylene, and toluene were procured from Spectrochem, India, N-bromosuccinimide (NBS 98%) from TCI, Japan, Trimethylamine (TMA 30%) from Qualigens, India and PVC (M_n 70,495, M_w 146,136) from National Chemical, India. These were used as received. Film grade high density polyethylene (HDPE, F-46) and linear low density polyethylene (LLDPE, F-19) were purchased from Reliance Industries, India.

2.2. Synthesis of p-MS-co-DVB based AEM

Two different types of anion exchange membranes of *p*-MS-co-DVB were prepared, one with PVC as binder (AEM-1 to AEM-6) and the other with PE (AEM-7). Their preparations are elaborated below.

2.2.1. Synthesis of p-MS-co-DVB/PVC based AEM

2.2.1.1. Preparation of p-MS-co-DVB/PVC inter-polymer film. A mixture of 6.3 g *p*-MS, 0.7 g DVB and 0.07 g BPO (1% *w/w* with respect to monomer mixture) was added into a solution of 3 g PVC in 30 mL of THF under constant stirring at 65 ± 1.0 °C for 4 h. The resultant hot solution was poured on a glass plate and the film was cast by ‘SS-304’ metal roller which resulted in uniform thickness. The operation was carried out in a closed casting chamber to avoid solvent inhalation and also for slow evaporation to avoid pin holes. No attempt was made to purge the chamber with nitrogen. The film was dried under ambient temperature for 12 h. Thereafter, it was peeled off from the glass plate and un-reacted monomer and solvent were removed through washing with methanol. Films were also prepared by varying the ratio of *p*-MS:DVB (total weight maintained at 7 g), keeping other conditions constant. The *p*-MS content in the film was computed from

$$\%p\text{-MS}(w/w) = 100 \times [\text{film wt.}-(\text{wt. of binder and DVB charged})]/\text{wt. of film} \quad (1)$$

Eq. (1) assumes that there is no loss in the binder and DVB amounts charged and the entire amount is recovered in the film. The equation further assumes that there is no residual solvent in the film after drying.

2.2.1.2. Bromination of p-MS-co-DVB/PVC inter-polymer film. Benzylic bromination of the inter-polymer film (25 cm × 25 cm × 0.015 cm) prepared above was carried out using NBS as brominating reagent (NBS:*p*-MS = 2.5–2.9 M ratio). The reagent and initiator were taken in 700–800 mL of pure and mixed chlorinated solvents (CCl_4; DCE; varying proportions of CCl_4+DCE) and the solution was poured into a cylindrical glass reactor. The inter-polymer film prepared above was immersed in the solution and allowed to react for 5–6 h at 75–80 °C under constant stirring in the presence of a 100 W tungsten lamp. The brominated film was then removed, washed with methanol and dried under ambient conditions. It was further dried under vacuum (4–5 mm Hg) at room temperature and its Br-content was analyzed by the Volhard method [35]. Similar procedure was followed for all the *p*-MS-co-DVB/PVC inter-polymer films. The yield of bromination was computed to a good approximation using

$$\text{Bromination yield}(\%) = [\%\text{Br}(w/w) \text{ in the film}/(\%\text{Br})_T(w/w)] \times 100 \quad (2)$$

wherein $(\%\text{Br})_T(w/w)$ is the theoretical Br wt% in brominated film for a given *p*-MS content of unbrominated film. $(\%\text{Br})_T(w/w)$ is expressed, in turn, by

$$(\%\text{Br})_T(w/w) = [100(W_{AB}-W_{BB})/W_{AB}] \quad (3)$$

wherein W_{BB} and W_{AB} correspond to the weights of the films before and after bromination with theoretical yield respectively.

2.2.1.3. Quaternization of brominated p-MS-co-DVB/PVC films. The brominated films were immersed in aqueous trimethylamine solution (30% *w/w*) in closed container at ambient temperature for 24 h. The contents were shaken occasionally. The resultant membrane was washed thoroughly with water to remove the adhering amine. It was thereafter conditioned by immersing in 1 M HC1 followed by water wash till neutral pH, followed by immersing in 1 M NaOH, followed by water wash till neutral pH once again. This cycle was repeated three times. The films were then kept standing in 0.1 M NaCl solution for 24 h. The adhering liquid on the membrane surface was wiped prior to measurement of membrane properties.

2.2.2. Synthesis of p-MS-co-DVB/PE based AEM

2.2.2.1. Preparation of p-MS-co-DVB/PE inter-polymer film. Inter-polymer of *p*-MS-co-DVB/PE was prepared at 5 kg scale through suitable modification of the hardware and literature procedure [36], and replacing styrene with *p*-methylstyrene. Details of the hardware, process optimization and characterization studies will be reported separately. Briefly, granules of F-46 HDPE (3.12 kg) and F-19 LLDPE (0.780 kg) were charged into a mixtruder equipped with sigma blade mixing arrangement. 1.25 L of xylene was then added and the mixture heated to 150 °C resulting in a homogeneous dough. 2.5 L toluene was added slowly into the above mass and temperature of the reaction chamber was lowered to 90 °C. At this temperature the mixture of *p*-methylstyrene (2.0 L), DVB (0.105 L), benzoyl peroxide (20 g) and toluene (0.5 L) was added into the organogel under high speed of mixing. The polymerization was continued for 4 h. After polymerization the temperature of the chamber was increased to 130–140 °C to recover the solvent from the polymer mixture. After recovering approximately 80–85% 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 a pelletizer. The inter-polymer pellets were kept in an oven 75–80 °C for 8 h to remove unreacted monomers and solvents. After curing, these were converted into thin films (0.24–0.28 mm) through blow film extruder. *Para* methylstyrene content in the film was computed based on Eq. (1). It was also determined from estimation of carbon content and the application of Eq. (4) below

$$\%\text{C in film} = 0.9152x + 0.923(0.1x) + 0.855(100 - 1.1x) \quad (4)$$

wherein x is the % (*w/w*) *p*-MS in the film, and the values of 0.9152, 0.923 and 0.855 correspond to the carbon weight fractions in *p*-MS, DVB and PE binder, respectively. The C % in film was experimentally determined on Vario Micro Cube elemental analyzer.