Preparation of a Mono-sheet Bipolar Membrane by Simultaneous Irradiation Grafting Polymerization of Acrylic Acid and Chloromethylstyrene

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ABSTRACT: A new type of mono-sheet bipolar membrane was produced from a porous polyethylene (PE) substrate using simultaneous irradiation grafting polymerization of acrylic acid (AA) on one side and chloromethylstyrene (CMS) on the other side. PE film with absorbent filter paper absorbing AA on one side and paper absorbing CMS on the other side was irradiated in the cobalt-60 gamma ray irradiation field, followed by quaternization with trimethylamine aqueous solution. AA and CMS were grafted on the substrate membrane simultaneously. The performance of the final membrane is significantly affected by the irradiation time. For short irradiation time, the prepared membrane behaves as a bipolar membrane; whereas for long irradiation time, the final membrane behaves as a charge mosaic membrane. Therefore, by controlling the conditions, a bipolar membrane with good current rectification can be prepared, across which the voltage drop is ~2.0 V at the current density 800 A/m^2 in 1.0 M NaOH. This preparation method is simple and can be applied both in laboratory and in industry. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 572–576, 2003

Key words: membranes; irradiation; graft copolymers

INTRODUCTION

A bipolar membrane, which consists of an anion-selective layer on one side and a cation-selective layer on the other, has been applied industrially in resources recovery, pollutants control, and chemical processing because of the simple process, high efficiency, and low wastes disposal.[1–6] There are many different methods to prepare a bipolar membrane, such as adhering an anion-exchange membrane and a cation-exchange membrane together with heat and pressure or with adhesive glue,[7, 8] as well as the casting of the solution of ion-exchange resin on oppositely charged ion-exchange membranes.[9–13] Further, a bipolar membrane can also be made from a single sheet of polymeric material by chemical reactions on the two sides to introduce cation- and anion-exchange groups.[14,15]

An important property of a commercial bipolar membrane is its high durability. A commercial bipolar membrane is blister free and degradation negligible for long periods of operation.[1] In general, a mono-sheet bipolar membrane, whose oppositely charged ion-exchange groups are chemically bonded to the substrate on the two opposite sides, has the higher durability compared with the bipolar membrane prepared by pressing or gluing or casting methods. To date, several methods for preparing a mono-sheet bipolar membrane are available. Dege et al. prepared mono-sheet bipolar membranes from pre-swollen styrenated films.[14, 15] Under controlled conditions, high dissociable cationic-exchange groups are chemically bonded to the aromatic nuclei to a desired depth of the film from one side only. Subsequently, highly dissociable anion-exchange groups are chemically bonded to the unreacted aromatic nuclei on the other side of the film. Yokoyama et al. developed another type of mono-sheet bipolar membrane.[16] Their preparation method was based on plasma-induced graft polymerization, which successively introduces different charged layers on either side of a porous polymer membrane.

In this article, a mono-sheet bipolar membrane was prepared from porous polyethylene (PE) film as a substrate by the irradiation graft polymerization of acrylic acid (AA) on one side and chloromethylstyrene (CMS, mixture of *para-* and *ortho-*isomers) on the other side simultaneously. PE membrane was used as the substrate because of its excellent material properties on which vinyl monomer is easily grafted. This work includes the synthesis of CMS and investigations of the irradiation processes and the performance of the prepared membranes.

EXPERIMENTAL

Materials

PE (H2200) was provided from Asahi Kasei Company, with a thickness of 200 μm, porosity of 70%, and max

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pore diameter of 0.3 μm. The specific area of the membrane was ~18 m^2/g, as determined by the Brunauer–Emmett–Teller (BET) adsorption method.[17] AA was chemically pure and provided by Shanghai Chemical Reagent Company. CMS, mixture of *para*- and *ortho*-isomers, was prepared in our lab (vide supra). All other chemicals were used as received.

Chloromethylstyrene was synthesized by the chloromethylation of 2-phenylethyl bromide, which was prepared from 2-phenylethyl alcohol by a halogenating reaction followed by dehydrobromination. Kondo et al described this procedure in detail.[18] Hydrobromic acid was used as halogenating agent, and hydrogen chloride and paraformaldehyde were used as chloromethylation agents. To improve the conversion in halogenating reaction and make the operation easy in the chloromethylation reaction, red phosphor and bromine and concentrated hydrochloric acid and phosphorus oxychloride replaced hydrobromic acid and hydrogen chloride in our synthesis. The mixture of *o*- and *p*-chloromethylstyrene was the desired product. Because both the isomers can be grafted on the membrane, there is no need to separate the isomers by column chromatography.

Preparation of membranes

PE film was cut into the square of 5 × 5 cm and washed repetitively with 0.1M sodium hydroxide and 0.1M hydrochloric acid aqueous solutions to make the surfaces clean. The PE film was dried before use. Two pieces of absorbent filter papers, respectively immersed in AA aqueous solution and CMS ethanol solution, were used to wipe away the drops of the surfaces and were placed on two thin glass plates. The PE film was located between two glass plates that
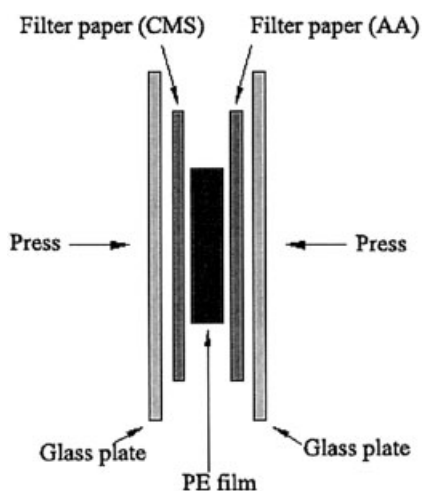

Figure 1 Schematic representation of sample preparation. Porous PE film was placed between absorbent filter paper absorbing AA and paper absorbing CMS and they were pressed together using two pieces of thin glass plates.
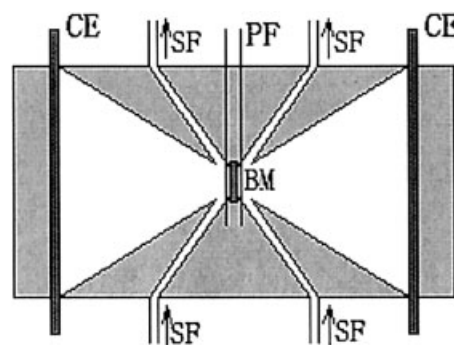

Figure 2 Current–voltage measurement apparatus. Key: (CE) current electrode; (PF) platinum filament; (SF) solution flux; (BM) bipolar membrane.

were pressed together using clamps with paper absorbing AA on one side of the PE film and paper absorbing CMS on the other side, as shown in Figure 1. This whole system was subjected to irradiation in a 60,000 Ci cobalt-60 source. Gamma rays from the cobalt-60 source induced the simultaneous grafting polymerization of AA and CMS on the opposite surfaces of the PE membrane. The grafted membrane was washed with ethanol to remove the homopolymers (poly-AA and poly-CMS) and immersed into 33% trimethylamine aqueous solution (TMA) at 50°C for 16 h to convert grafted CMS to quaternary ammonium. The prepared membrane consists of grafted AA as the cation-exchange layer and grafted CMS followed by quaternization as the anion-exchange layer.

For the measurements of grafting degree and Fourier transform infrared (FTIR) spectroscopy, the grafting of AA and CMS was also conducted separately under the same conditions as the simultaneous grafting just described.

Characterizations of the membranes

The final membranes were characterized by ion exchange capacity (IEC), degree of grafting, FTIR and current–voltage curve (I–V curve) measurements. IEC was determined by conventional acid–base titration. The degree of grafting was determined as follows:

$$\text{Degree of grafting (\%)} = (W_g - W_0)/W_0 \times 100 \quad (1)$$

where W_g and W_0 are the weights of the film after and before grafting, respectively. FTIR spectra measurements were made with a Bruker Vector 22 FTIR spectrometer using OPUS software for data collection. All the spectra were recorded at 4 cm^{-1} resolution with a zero filling factor of 4 and with averaging 100 interferometer scans. The I–V curve was collected as explained next.

The I–V curve measurement apparatus for the prepared membrane is shown in Figure 2. It is similar to

TABLE I
IEC and Grafting Degree for M220 and M520 Membranes

Membrane	Anion IEC (meq/g dry)	Cation IEC (meq/g dry)	CMS grafting degree (%)	AA grafting degree (%)
Native PE	Undetectable	Undetectable	Undetectable	Undetectable
M220	0.15	0.72	8	13
M520	0.25	1.32	14	25

the one reported in literature,[19] but slightly different with regard to current electrodes, measurement electrodes, and directions of the solution flux. The measurement cell has a conical shape, which gives a large surface for the current electrodes and a small area for the membrane, to minimize border effects and make the current through the membrane approximately homogeneous. The membrane of cross-section area 1.04 cm^2 was fixed between the two half-cells. The electrolyte solution in the super thermostatic bath was pumped at a constant flux from the bottom into the cell, and the streams were directed to the membrane surfaces to minimize boundary layer effect as well as to provide the necessary mixing of the solution. Both streams leaving each corresponding half-cell from the top were cycled to the super thermostatic bath, so the pH value of the whole solution was maintained constant. Two kinds of electrolyte solution, $1.0M$ NaOH and $0.5M$ Na$_2$SO$_4$, were used. The current was supplied by stabilized current DC power system (DF1731SD2A, Ningbo Zhonghua Electronics Company, Ltd.), measured with a multimeter (DT9205, Zhangzhou Mater Electronics Company, Ltd.), and introduced into the cell with two ruthenium plated titanium electrodes. The potential was measured with a multimeter (UT30B, Shengzhen Uni-Trend Electronics Company, Ltd.) by two platinum filaments located at ~1.0 mm in front of each membrane surface after having operated for 40 min at the current density of 300 A/m^2 to allow a quasi-stationary state to be established.

RESULTS AND DISCUSSION

Two pieces of membranes were prepared. The irradiation dose rate for grafting polymerization was 45 Gy/min, and the temperature was 25°C. One piece of membrane was prepared by the following procedure: grafting polymerization for 110 min, replacing the used filter papers by the new filter papers, grafting polymerization again for 110 min, and quaternizing. So, the total grafting polymerization time was 220 min, with a total dose of 9.9 kGy, and the membrane was denoted as M220. The other membrane, M520, with a total grafting polymerization time of 520 min and a dose of 23.4 kGy, was made by first using the procedure used to prepare M220, but without quaternizing, and then grafting polymerization for 150 min,

replacing the used filter papers by the new filter papers, grafting polymerization again for 150 min, and quaternizing. To improve the grafting degree, the grafted monomers must be diluted to the same extent so that there is no apparent homopolymerization under the irradiation dose. Our preliminary experiments showed that AA is easier to homopolymerize than CMS, so in our experiments, AA was diluted as 33.3% (v/v) aqueous solution with $0.02M$ CuSO$_4$ as the inhibitor, and CMS as 50% (v/v) ethanol solution without any inhibitor.

The grafting reactions can be proved by measurement of ion-exchange capacities (IEC), degree of grafting, and the FTIR spectra. As shown in Table I, both M220 and M520 have some amount of cation IEC and anion IEC, which indicates the successful grafting polymerization of AA and CMS on their respective sides. It is also evident that both IEC and grafting degree of the cation layer (AA layer) are higher than those of the anion layer (CMS layer), mainly because AA is more easily grafted on the PE film than CMS under the grafting conditions used. Therefore, in practical membrane preparation, we chose a relatively lower concentration for AA. The effect of irradiation time on grafting process can be obtained by comparing membrane M220 with M520. Obviously, the longer the irradiation time, the higher the grafting degree and thus the higher the IEC.

Further evidence of the grafting process is found in the results of FTIR analysis. As an example, the FTIR spectra of the substrate PE film, AA-grafted PE film, CMS-grafted PE film, and the simultaneous AA- and CMS-grafted PE film are shown in Figures 3(a–d), respectively. In the range 1800–600 cm^{-1}, the substrate PE film [Fig. 3(a)] has two apparent absorption bands at 1463 and 720 cm^{-1}. A difference observed between AA-grafted PE film [Fig. 3(b)] and the substrate [Fig. 3(a)] at 1716 cm^{-1} is assigned to the C=O stretching vibration in carboxylate group. The two absorption bands at 1608 and 1490 cm^{-1} in the spectra of CMS-grafted PE film [Fig. 3(c)] belong to the stretching vibration of the carbon—carbon bond in the phenyl ring, and the absorbency between 900 and 600 cm^{-1} shows the existence of *para-* and *ortho*-substituted phenyl rings. The IR spectra of the membrane [Fig. 3(d)] also verify the grafting polymerization of AA and CMS on the substrate.
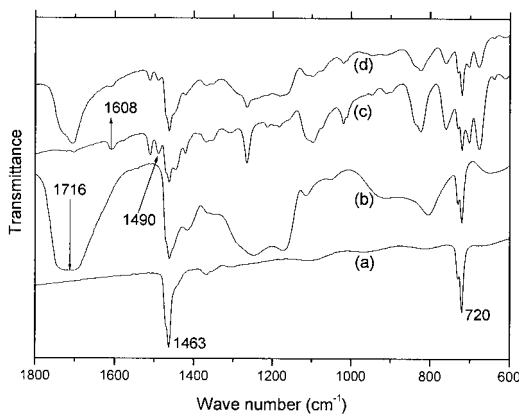
Figure 3 The FTIR spectra of the (a) the substrate PE film, (b) the PE film grafted with AA, (c) the PE film grafted with CMS, and (d) the PE film grafted with both AA and CMS.

The I–V curve is one of key characterizations of a bipolar membrane and can provide valuable information concerning the membrane.[1, 19] The I–V curves of the final membranes M220 and M520 under forward and reverse polarization are shown in Figure 4. The curve of M220 shows the typical current rectification, which is characteristic of ordinary bipolar membrane and is often discussed in term of p–n junction in semiconductors. The curve is convex to the voltage axis under reverse polarization because at reverse voltage, the junction is depleted of salt ions and most of the current is carried by the H^+ and OH^- ions generated by the water splitting and increases rapidly with the voltage. The membrane resistance then decreases with the applied voltage, and the slope of the curve increases.

In contrast, the I–V curve of the membrane M520 is linear on the whole and does not show the obvious current rectification or water-splitting effect. A comparison of the two curves allows acquisition of some details of the grafting polymerization. As already mentioned, the substrate of the prepared membranes was a porous PE film with a porosity of 70% and a maximum pore diameter of 0.3 μm.[17] When the PE film with absorbent filter paper absorbing AA on one side and paper absorbing CMS on the other side was irradiated, AA and CMS were grafted onto the membrane from the opposite surfaces simultaneously. At the same time, AA and CMS were partially homopolymerized, and to a certain extent the homopolymers on the surfaces restrained the monomers from entering into the insides of the membrane and being grafted in the inside. But the partial in-leakage of the monomers was unavoidable because of the porosity of the substrate PE film. The grafting depth of AA and CMS increases with an increase in irradiation time because of penetration of monomers into the membrane. However, it will take some time for the monomers to diffuse into the whole membrane depth. If

time is not sufficient, the diffusive distance of the monomers into the substrate is short. In this case, the two kinds of monomers will not penetrate each other significantly, leaving a relatively clear boundary between the anion- and cation-exchange layers. Our preliminary experiments show that the monomers will not interfere with each other significantly if the irradiation time does not exceed 250 min. So, before this time, the cation-exchange layer obviously will not overlap with the anion one after grafting. This situation is why the M220 membrane shows the typical behavior of an ordinary bipolar membrane. For the M520 membrane, according to our previous analyses and because the time is too long, the monomers will penetrate into most depths of the substrate. After grafting, both the cation- and anion-exchange layers will penetrate each other, especially in the intermediate part of the substrate. In this case, it is easy to form a charge mosaic membrane in which both positive and negative fixed charge groups are interdistributed in the membrane bone. The approximately linear curve of the M520 membrane indicates that it is more like a charge mosaic membrane than a bipolar membrane and it has low permselectivity.

Thus to prepare a bipolar membrane with perfect performances in this simultaneous irradiation grafting polymerization method, the thickness of the two ion-exchange layers should be controlled to make the two layers connected to each other exactly or only overlap each other a little. In other words, the rate of the monomer diffusing into the substrate and being grafted onto the substrate should be controlled. To achieve this goal, three factors should be considered. (1) A membrane with low porosity and small pore diameter or a dense membrane as the substrate can reduce the diffusion rate, which makes it possible that the monomers are grafted primarily on the surface. (2) Prolonging the irradiation time will lead to increasing penetrating depth, which means a larger grafting layer
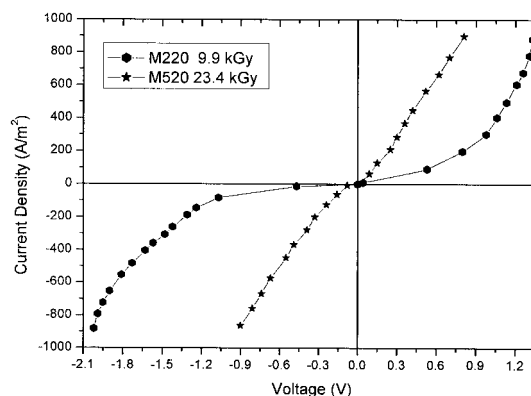

Figure 4 Current–voltage curves of the prepared M220 (●) and M520 (☆) membranes using 1.0M NaOH as the electrolyte at 30°C.
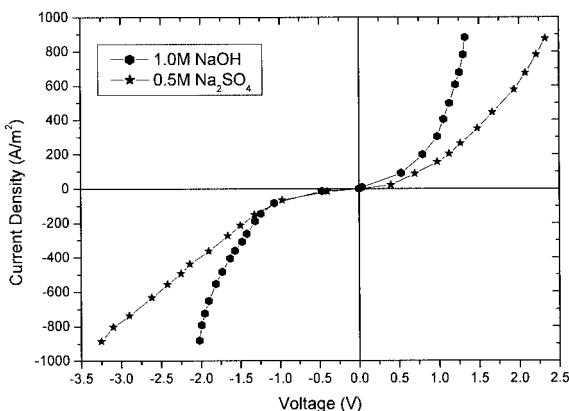
Figure 5 Current–voltage curves of the prepared M220 membrane using (●)1.0M NaOH and (☆) 0.5M Na$_2$SO$_4$ as the electrolyte at 30°C.

thickness. (3) The grafting polymerization of two kinds of monomers proceeds simultaneously and competitively towards the opposite side. The concentration of the grafting solution affects the diffusion rate and grafting rate of the monomers. By controlling the concentrations, the bipolar membranes with different thickness of the two ion-exchange layers are expected.

The I–V curves of the M220 membrane, using 1.0M NaOH and 0.5M Na$_2$SO$_4$ as the electrolytes are shown in Figure 5. The M220 membrane consists of a weakly acidic cation-exchange layer (AA grafted) and a strong basic anion-exchange layer. In neutral Na$_2$SO$_4$ solution, the weakly acidic AA-grafted layer dissociates only partially, which incurs the high resistance and low permselectivity. The voltage drop across the M220 membrane under reverse polarization is ~3.1 V at the current density 800 A/m^2 in 0.5M Na$_2$SO$_4$, and ~2.0 V in 1.0M NaOH. This kind of bipolar membrane, with a weakly acidic cation-exchange layer, is expected to have an excellent performance when it is applied in basic solution.

CONCLUSIONS

A new method is proposed for making a mono-sheet bipolar membrane from a porous PE substrate using irradiation graft polymerization of AA and CMS. The performance of the prepared membrane is significantly affected by the irradiation time. Using porous PE film as the substrate and proper concentrations of AA and CMS, for short irradiation times, the prepared membrane behaves as a bipolar membrane. In contrast, for long irradiation times, the final membrane

behaves as a charged mosaic membrane. The prepared bipolar membrane shows a good current rectification. The voltage drop across the bipolar membrane is ~2.0 V at 800 A/m^2 in 1.0M NaOH.

The method possesses two main characteristics: (1) ion-exchange groups are grafted on the substrate by irradiation-induced grafted polymerization, and (2) cation- and anion-exchange layers are formed simultaneously. This method has wide applicability. According to the general irradiation theory, most vinyl monomers can be grafted on polyolefin membrane easily under certain conditions.[20] With the exception of AA and CMS, other vinyl monomers (e.g., as styrene sulfonic acid, styrene trimethyl ammonium chloride, vinylpyridine, etc.) also can be used to prepare bipolar membranes. Further research will be focused on the effect of the porosity of the substrate on membrane properties.

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