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Proton exchange membranes prepared by radiation-induced graft copolymerization from binary monomer mixtures onto poly(tetrafluoroethylene-co-hexafluoropropylene) film

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ABSTRACT

Sulfonic acid proton exchange membranes based on a poly(tetrafluoroethylene-co-hexafluoropropylene) film were synthesized through the single-step graft copolymerization of sodium styrenesulfonate and acrylic acid monomers from binary monomer aqueous solutions using the electron beam pre-irradiation method in air. The effects of the various polymerization parameters (absorbed dose, reaction time, and monomer ratio) on the degree of grafting were studied.

A correlation between the degree of grafting and some of the physical–chemical properties (water uptake and ion-exchange capacity) of the synthesized copolymers was established. The distribution of the sulfonic acid groups was investigated across the thickness of several membranes in order to gain a better understanding of the graft copolymerization process from binary monomer aqueous solutions onto the fluorinated film and to synthesize membranes with optimal physical–chemical properties.

1. Introduction

Radiation-induced graft polymerization is an attractive technique for the synthesis of chemically active polymer films. This method allows to introduce functional groups into a preformed polymer film by grafting of a monomer with a desirable functional group or to graft the chains of a precursor-monomer followed by polymer-analogous transformations [1].

The advantages of the radiation-induced graft polymerization method include its low cost and simplicity. Additionally, commercially available (preformed) films can be used as the polymer backbone, and the grafting of secondary polymer chains is easy and controllable. Therefore the properties of the synthesized copolymers can be tailored to the demands.

The radiation-induced graft polymerization can be applied to synthesis of solid polymer proton exchange membranes for fuel cells, and this use has widely been studied over the last decade [2–6].

Although both hydrocarbon and fluorocarbon polymers can be used as the base film for the fuel cell membrane synthesis, the latter is the most perspective material because of their good mechanical strength, chemical and thermal resistance, and various properties that can be easily modified using the grafting method.

Almost all of the commercial available fluorinated polymers, such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP), poly(vinylidene fluoride) (PVDF), ethylene–tetrafluoroethylene copolymer (ETFE), etc., have been tested as base polymers for the synthesis of proton exchange membranes for fuel cells. The radiation grafting of the styrene monomer and the subsequent sulfonation of the polystyrene grafted chains is mainly used for synthesize of these proton exchange membranes [2–5].

Although proton exchange membranes can be synthesized through the radiation grafting of monomers containing sulfonate groups (for instance, sodium styrene sufonate – a vinyl monomer with sulfonate group), only a few publications have examined this technique [7–12].

In a previous study a cation-exchange adsorbent was prepared through the single-step graft copolymerization of sodium styrenesulfonate and acrylic acid monomers from binary monomer mixtures onto a nonwoven polypropylene fabric [10]. The high adsorption characteristics of the resultant fabric and simple the single-step synthesis have made this approach plausible for the synthesis of proton exchange membranes for fuel cells. However there are no publications on synthesis of proton exchanger membranes based on fluorinated polymers by such approach.

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In this work sodium styrenesulfonate (SSS) and acrylic acid (AA) monomers were graft polymerized from aqueous monomer solutions onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films using the electron beam pre-irradiation method in air.

At the first stage of our investigation the grafting of AA + SSS monomers onto the FEP films was carried out at the moderate temperature (50 °C) without any inhibitors to understand the peculiarities of this reaction.

The effects of the various polymerization parameters (monomer mixture ratio, absorbed dose, and reaction time) on the degree of graft copolymerization at 50 °C were considered.

A correlation was established between the degree of grafting and some of the physical–chemical properties of the synthesized copolymers. The distribution of the sulfonic acid groups across the thickness of several membranes was also investigated in order to gain a better understanding of the graft copolymerization process from binary monomer aqueous solutions onto FEP film and to synthesize.

2. Experimental

2.1. Materials

The FEP film with a thickness of 125 μm was purchased from Du Pont and used as the base polymer for the synthesis of polymer electrolyte membranes.

Reagent grade acrylic acid ($CH_2{=}CHCOOH$, Aldrich) and sodium styrenesulfonate ($CH_2{=}CHC_6H_4SO_3Na$, Aldrich) were used as received. Reagent grade methanol, acetone, and 0.1 N NaOH (Duksan Pure Chemicals Co., Ltd., Korea), were also used in the experimental work.

2.1.1. Graft copolymerization procedure

The pre-irradiation grafting technique was carried out in air for the graft copolymerization from the SSS + AA monomer aqueous solutions. The FEP film was cut into 50 × 50 mm quadrates, cleaned with acetone for 24 h and then dried at 80 °C for several hours before being weighted. The prepared samples were irradiated with an electron beam from an ELV-05 electron beam accelerator (BINP, Russia) with an accelerated energy of 0.7 MeV to doses ranging from 40 to 100 kGy at ambient temperature.

The irradiated film (about of 0.7 g) was immersed in a 250 ml glass flask with the monomer (s) water. Then the flask was purged using nitrogen gas, sealed, and placed in a water bath that was maintained at a constant temperature of 50 °C for different time periods. At the end of this stipulated time period, the grafted FEP films were removed from the solution, washed thoroughly with hot distilled water (for 6 h) and water–methanol solution (for 12 h) to remove any homopolymers and unreacted monomers, and then washed with distilled water several times. Finally, the grafted films were dried in a vacuum oven at 80 °C until they reached a constant weight. The degree of grafting (DG) was calculated from the weight gain:

$$\text{DG}\ (\%) = [(W_1 - W_0)/W_0] \times 100,$$

where W_0 and W_1 are the weights (g) of the original and grafted films, respectively.

At least three samples were investigated for each experimental point.

2.1.2. FT-IR analysis

The FT-IR–ATR measurements were carried out using a spectrum 100 FT-IR spectrometer (Perkin–Elmer) in the transmittance mode. Spectra were collected by cumulating 12 scans.

2.1.3. Microprobe measurements

The energy dispersive X-ray spectroscopy (EDS) of the sulfur was used to examine several cross-sections and horizontal sections of the dry membranes using a Hitachi S-4100 field emission scanning electron microscope (FE-SEM) at acceleration voltage of 15 keV. The samples were sputter coated with a thin Pt layer prior to examination.

2.1.4. Water uptake

The water uptake of the obtained membranes was determined by placing them in deionized water at room temperature for 24 h until the water absorption equilibrium was reached. Then the membranes were removed, placed on the filter paper to remove the excess surface water and weighed. The water uptake was calculated using the follows equation:

$$\text{Water uptake}\ (\%) = [(W_w - W_d)/W_d] \times 100,$$

where W_w and W_d are weights of the wet and dry membrane, respectively.

Each experiment was repeated three times.

2.1.5. Ion-exchange characteristics

The ion-exchange capacity (mEq/g) of the synthesized membranes was determined through backward titration experiments. The grafted FEP film (about 0.2 g) was completely converted into the H^+ form through treatment with an excess solution of 0.1 M HCl for 24 h. The sample was washed, dried and weighed before being placed into a flask with 20 ml of a saturated NaCl solution and equilibrated for 24 h. The equilibrated solution was titrated to the phenolphthalein end point with 0.1 N NaOH solution using TITRONIC 97/50 auto burette.

The IEC value of the membrane was calculated using the following equation:

$$\text{IEC (mmol/g)(mEq/g)} = 0.1 \times V_{\text{NaOH}}/W_d,$$

where, V_{NaOH} is the volume of NaOH solution that was consumed during titration, and W_d is the weight (g) of the dry membrane in the H^+ form. Each experiment was repeated three times.

3. Results and discussion

The sulfonic acid proton exchange membranes on the FEP film were synthesized through the single-step graft copolymerization of the sodium styrenesulfonate and acrylic acid monomers from binary monomer mixtures using the electron beam pre-irradiation method in air.

A previous study [10] showed that the copolymerization process from the AA + SSS monomer mixtures onto the polypropylene fabric began through the grafting of the acrylic acid monomers. One possible mechanism for the copolymerization process suggested that the initial grafting of the AA monomers imparted hydrophilic properties onto the polymer surface, which was originally hydrophobic, facilitating the further grafting of the SSS monomers.

Similar to previous reports [7,8] the SSS monomers could not be grafted onto FEP films from the monomer aqueous solutions at various irradiation doses, times and temperatures. However, the copolymerization of SSS was successfully accomplished in a mixture with AA.

The effects of the experimental parameters on the degree of grafting were investigated and correlations between some of the physical–chemical properties of the synthesized membranes and the DGs are presented below.