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Copolymerization of Styrene onto Polyethersulfone Films Induced By Gamma Ray Irradiation

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Summary

Radiation-induced grafting of styrene into polyethersulfone (PES) films were investigated by simultaneous method in solution using gamma-ray from a radio nuclide ^{60}Co source. The starting materials were prepared via casting method of the polymeric solution. The grafted membranes have side chains of polystyrene which may be sulfonated to become proton conductive to be used as polymer electrolyte membrane in fuel cell. The localized energy of high intensity gamma-ray induced breaking of chemical bonds leads to free radical formation, a reactive species having a single unpaired electron. The radical start a conventional polymerization sequence comparable with that obtained with a chemical catalyst acting as initiator. The effects of grafting conditions include monomer concentration, irradiation total dose, dose rate and addition of cross linking agent, were studied by means of the techniques of structure analysis, morphology, thermal degradation and crystallinity. The degree of grafting (DOG) was analyzed by percentage of the weight increase. As a result, the reaction always follows the same pattern: DOG increases rapidly initially whilst propagation is the main reaction, then more slowly as termination becomes more frequent.

Introduction

Radiation grafting has been investigated for many years with the objective to prepare polymeric ion exchange membranes for fuel cells and other electrochemical applications. The advantages of radiation-grafted membranes include lack of need for chemical initiators or catalysts, the easy preparation from already prefabricated base film, and easy control of the degree of grafting. A major motivation for most of the recent work in this field has been to find lower-cost alternatives to perfluorinated, Nafion®-type membranes which have been difficult to be used in large-scale commercial applications [1]. PES is a high-performance engineering thermoplastic and its high glass transition temperature (225°C) and polar structure with phenyl rings brings superior mechanical and thermal properties [2,3]. Then, PES is an interesting material to be used as base polymer in polymer electrolyte membrane as hydrophobic host that constrains the membrane swelling in water and provides mechanical stability.

Copolymers of PES have been prepared by γ-ray irradiation with one or more monomers that react with a base polymer forming side chains. Typically binary monomers of styrene/divinylbenzene (DVB) have been used because the monomers units can be easily sulfonated to introduce sulfonic acid groups into the membranes [4,5]. The bifunctional monomer DVB is used as cross linker to improve the chemical stability of the radiation-grafted membranes [6]. The objective of this work is to obtain PES grafted with polystyrene, in order to produce membranes with special properties (Figure 1).

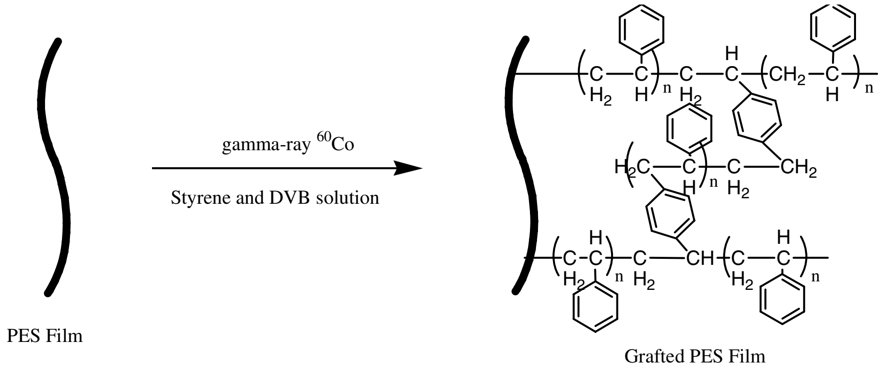

Figure 1. Preparation of grafted PES membrane by gamma-ray irradiation

Experimental

Materials

Divinylbenzene-DVB and styrene, were kindly provided by Petroflex (Rio de Janeiro). DVB was used as received. Styrene was distilled under reduced pressure (10^{-5} mmHg). Polymer Polyethersulfone (PES) - was provided by BASF, Density (d 20^{o}C/ 4^{o}C) - 1,37; M_w=58.000; T_g=225 ^{o}C. All other chemicals obtained commercially were reagent-grade and used as received.

Preparation of PES membranes

The commercial polyethersulfone was dissolved in N-N-dimetilformamide (DMF) to obtain a 18 wt % PES solution. The polymer was kept 8 hours in contact with the solvent and dissolution was completed with mechanical stirring at 60 ^{o}C of temperature. The solution was filtered with a cellulose acetate membrane and cast onto a glass plate and then dried completely in vacuum oven at 60 ^{o}C. PES membranes of 100 μm thickness were obtained.

Grafting Procedure

The PES film was cut into pieces (2 x 3 cm^2) and dried in a vacuum oven (10 mbar) at 60 ^{o}C. The dried film was precisely weighted and placed in a glass reactor immersed into a styrene and divinylbenzene solution of known concentration. The grafting solution was bubbled with dried nitrogen for 5 min at a flow rate of 10 l/h to remove all oxygen in the vessel and create an inert atmosphere. After that, the reactor was sealed with an elastomeric material. The irradiation was carried out at a MDS Nordion, model Gammacell 220 Excel gamma ray source at ambient temperature for required period of time. Once grafted, the films were washed in toluene to remove homopolymerised styrene, prior to drying to constant weight in an oven at 60 °C. The degree of grafting (DOG) was gravimetrically determined as a percentage of the weight increase of PES film using the equation (1):

$$\text{DOG}\ (\%) = \frac{W_g - W_o}{W_o} \times 100 \qquad (1)$$

where W_g and W_o are the weight of the grafted and original PES films, respectively. The DOG therefore represents the proportion of the copolymer which is grafted material [7,8].

Characterization and Measurements

FTIR measurements were carried out using a Perkin-Elmer (FTIR 1720-X) spectrometer with 20 scans and 2 cm^{-1} of resolution. The spectra were recorded for base polymer and grafted polymer films in the wave number range of 1600-3500 cm^{-1} and analyzed using commercial software.

The morphology study of the PES films grafted with polystyrene was carried out using a JEOL Scanning Electronic Microscopy (JSM-5610LV) with 10 to 20 KV of voltage acceleration. The secondary electrons imaging (SEI) used is an effective tool for examining surface topography in plan view, offering excellent resolution with a large depth of focused field. The samples were cryogenically fractured with liquid nitrogen and sputtering coating with a thin metallic gold film (~100 Å).

All grafted and irradiated samples, as well as the neat PES were analyzed by Shimadzu TGA-51, in order to characterize their thermal decomposition. Typical samples weighing 10 mg were used. Thermograms were obtained in a temperature range of 30-800 °C at constant heating of 20°C/min under nitrogen atmosphere at a flow rate of 20 ml/min.

Results and discussion

Grafting Reaction

The polymer films were irradiated to total doses of 5, 10, 15, 20, 25 and 30 kGy at dose rate of approximately 4,2 $kGyh^{-1}$. The grafting solution were made up using styrene concentration in methanol of 20%, 40% and 60% v/v. Figure 2 shows the DOG variation of polystyrene onto PES films with the monomer concentration. As can be seen, the DOG increases with increase in the irradiation total dose. The best results were achieved into irradiation total dose of 30 kGy for all studied monomer concentration. This behavior can be attributed to the increase in the number of radicals formed in the grafting system [3]. There is a general trend that as the monomer concentration increases then the DOG increases. In some cases, after a certain concentration, a plateau is reached and increasing the monomer concentration gave any increase in grafted yield. In the irradiation total dose of 30 kGy, the best results were achieved to 40% monomer concentration. This may be because the grafting reaction takes place via front mechanism. The monomer concentration affects the availability of the monomer reach the reaction sites on the polymer. When the number of monomer groups per grafting site is at its maximum, then the excess monomer may start to homopolymerise, causing the reaction mixture to become more viscous and hence limiting the mobility of unreacted monomer, not allowing it to reach the radicals formed within the polymer [9,10].

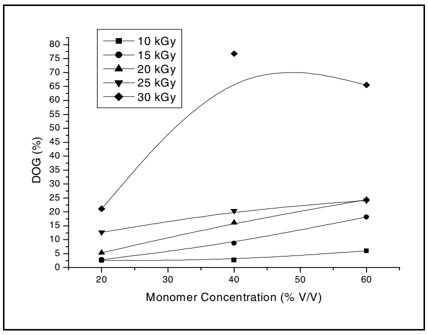

Figure 2. DOG variation of polystyrene onto PES films with the monomer concentration in different total doses

Morphology

Morphological investigations of graft copolymer of polystyrene onto PES film were performed by SEM. The microphotographs shows the top of fractured grafted membrane with DOG of 8,75 and 16,13%, Figure 3 (A) and (B), respectively, with the grafted layers of polystyrene in both sides of the membrane [8,11]. The reaction can occur simultaneously both on the outer surface of the substrate membrane and on the inner surfaces of the membrane pores, by initiation of the radicals formed inside with gamma-ray irradiation graft technology. However, as can be seen in Fig. 3 (B), only few nanometers of the substrate react to form side chains of polystyrene [12].

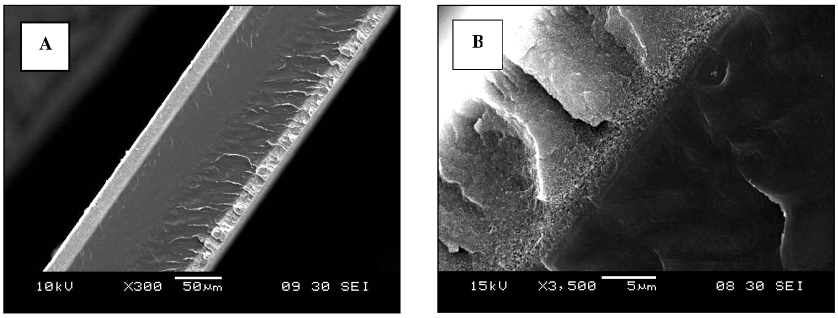

Figure 3. SEM micrograph of PES-g-polystyrene membrane having DOG of 8,75% (A) and 16,13% (B). Image of the top of fractured membrane

The reaction solvent used is important to permit the adequate swelling of the membrane substrate to obtain graft polymerization deeper inside the membrane. The surface study of graft membrane in Fig. 4 shows the domains of polystyrene heterogeneous distributed with average grain size below 3 μm. The gamma-ray treatment of the membrane induce a free radical formation and graft polymerization grow from those radicals. The grain size of the graft polystyrene is limited by the number of formed radicals on the substrate.

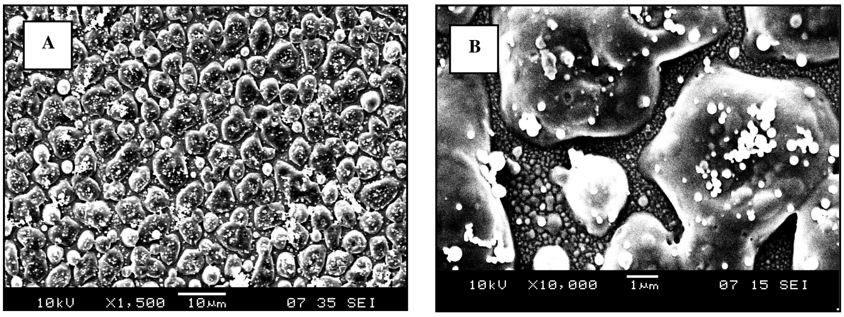

Figure 4. (A) and (B), SEM micrograph of the surface PES-g-polystyrene membrane having DOG of 8,75%

FTIR

Infrared spectroscopy allowed us to check the effectiveness of copolymerization. Figure 5 shows the FTIR spectra of grafted PES membranes with different degree of grafting gravimetrically calculated. 1) DOG=5,6%; 2) DOG=9,3%; 3) DOG=14,8%; 4) DOG=27,5%; 5) DOG=40,21% and 6) DOG=36,5%. It shows, after the grafting reaction, the presence of two bands at 2846 and 2920 cm^{-1}, which are characteristics of symmetric and asymmetric stretching vibrations, respectively, of polystyrene CH_2 groups. The steady increase of these bands makes it suitable for quantitative determination of the degree of grafting. For quantitative analysis of IR spectra of membranes, the band absorbance needs to be "normalized" to correct the changes due to non-uniform thickness among the samples [2,13-16].

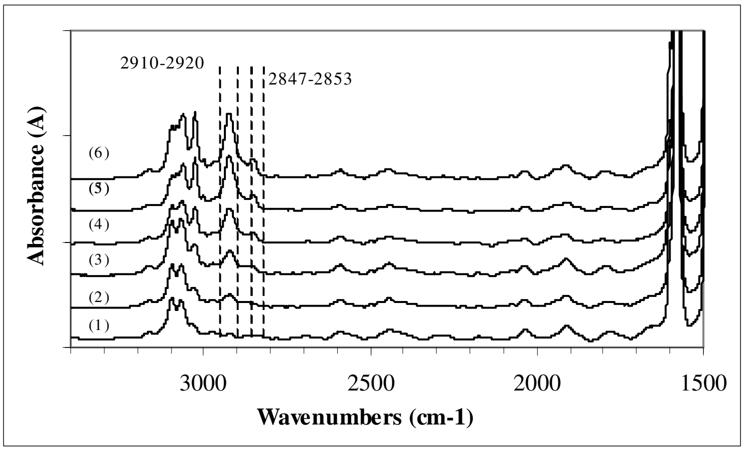

Figure 5. FTIR spectra of PES-g-polystyrene films having various DOG: (1) 5,6%; (2) 9,3%; (3) 14,8%; (4) 27,5%; (5) 40,21%; (6) 36,5%

Thermal Property

The thermal stabilities of PES were studied by TGA. In Figure 6, TGA analysis results are reported for PES pellets samples (1) and PES neat membrane (2) compared with irradiated PES membrane (3), irradiated in methanol with 10 kGy of gamma-ray. The PES is a highly thermo stable polymer. The PES pellets degradation curve (1) shows two weight loss steps, first 58wt% loss temperature around 590 °C and the second 40wt% loss around 680 °C, that is ascribed to the decomposition of polymer main chain. For the neat and irradiated membranes, (2) and (3), respectively, three transitions of loss in weight in three separate temperature ranges can be distinguished in the figure. The first step around 255 °C is associated to residual solvent DMF into the membrane. The neat and irradiated membrane shows the same decomposition curve pattern. The major difference is the dislocation of the irradiated membrane curve to lower temperature of thermal degradation which can be attributed to partially degradation of the membrane by irradiation. The irradiation main effect on PES membranes are scissions on C-O and C-S bonds producing volatile SO_2. The excess exposure of PES membranes to gamma irradiation tends to poor their properties [2,17,18].

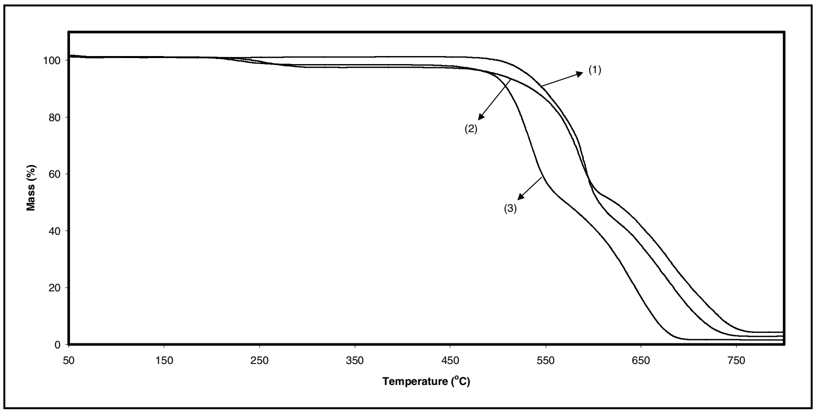

Figure 6. TGA traces of PES pellets (1), neat PES membrane (2) and irradiated PES membrane (3)

Conclusions

The experiments described above show that PES can be used as starting polymer for radiation-grafted membrane and, after that, be sulfonation to become ion-exchange membrane. Under suitable reactions conditions, the DOG may be controlled, to some extend, by varying the monomer concentration, total dose of radiation, type of solvent used and addition of the cross linker agent. The success of the reaction was confirmed by the FTIR, SEM and TGA analyses.

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