Preparation of proton exchange membrane by radiation-induced grafting method : Grafting of styrene onto poly(ethylene tetrafluoroethylene) copolymer films

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Abstract

Radiation induced grafting of styrene onto poly(ethylene-tetrafluoroethylene) (ETFE) copolymer film was carried out to prepare graft copolymer (ETFE-g-polystyrene) that can host sulfonic acid groups and form proton exchange membrane for polymer electrolyte fuel cell (PEFC). The effect of monomer concentration and type of solvent on the degree of grafting was investigated. The formation of graft copolymer film was confirmed by FTIR spectrum analysis.

Keywords : radiation-induced graft copolymerization; styrene; ETFE films

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1. Introduction

Many efforts have been devoted to develop proton exchange membranes by radiation-induced grafting technique (3-11). The attractiveness of this technique arises from its flexibility of using any type of radiation, such as gamma rays and electron beam irrespective of the shape and size of the polymer. The graft copolymer membranes offer a unique concept of combining desirable properties of two polymeric components. The attractive feature of the grafting process is that the amount of grafted component can be easily controlled by the proper selection of the irradiation as well as reaction parameters. As a result, the membranes with desired physico-chemical properties may be tailored.

In this process, polymer films is irradiated by high energy radiation and the irradiated films is allowed to react with vinyl monomer units which propagate to form grafted copolymer that have to be functionalized. For stability reason, fluorinated polymers are often used as base polymer and styrene is used as a grafting monomer that allows incorporation of sulfonic acid group. Partially fluorinated polymer film has advantages over fully fluorinated in term of radiation such as ETFE that permit the use of high dose and dose rate during the membrane preparation (3-4). Radiation grafting of ETFE films has been studied by several authors (3-10).

In this work, we report on preparation of grafting copolymer film by radiation grafting of styrene onto ETFE films which will be later hosting for sulfonic acid. The

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effect of reaction parameter such as monomer concentration and solvent on the degree of grafting was studied.

2. Experimental

2.1. Materials

Ethylene-tetrafluoroethylene (ETFE) films supplied by Goodfellow, Cambridge having thickness of 125µm and density 1.9gm/cm^3 were used for grafting. Styrene of purity more than 99% (Fluka) were used without further purification. Other chemicals like solvents were used as received.

2.2. Graft polymerization

The films were washed with ethanol, dried at 70^{o}C in vacuum oven, weighed and then irradiated using electron beam accelerator (Curetron, EBC-200-AA2) at 100kGy in nitrogen gas atmosphere. The irradiated films were then stored at –20^{o}C. The grafting reaction was carried out in glass ampoule at temperature 60^{o}C under nitrogen atmosphere with different solvent. After four hours grafting, the films were removed, rinsed with toluene, dried under vacuum at temperature 60^{o}C and weighed until constant weight. The degree of grafting was determined by weight increase as follows:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

Where W_o and W_g represent the initial and grafted weight of the films, respectively.

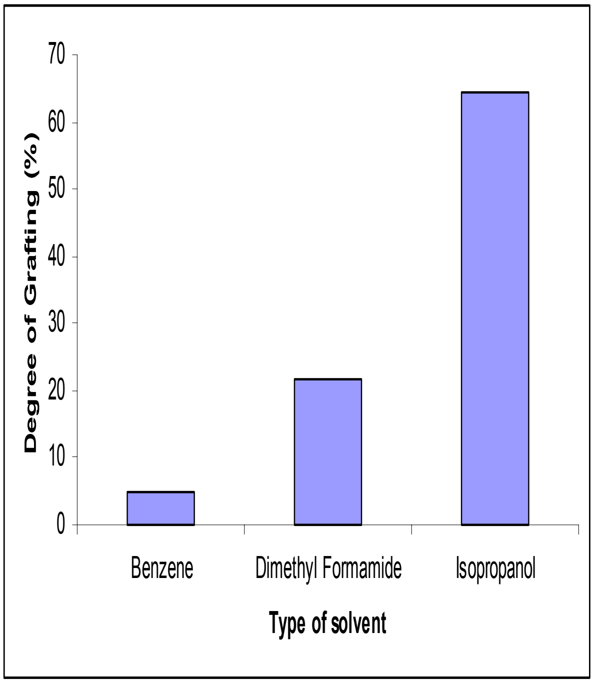
2.3. FTIR spectrometry

FTIR measurements were carried out using an FTIR spectrometer (Perkin Elmer Spectrum 2000) equipped with ATR. The spectra was measured in a range of 3600 to 600 cm^{-1}.

3. Results and discussion

3.1. Effect of solvent

The effect of different solvents on the graft copolymerization of styrene onto ETFE films was investigated and shown in Fig. 1. It can be seen that the dilution of styrene with presence of isopropanol leads to a remarkable degree of grafting compared to the dilution with benzene at 50 vol% of styrene/solvent mixture. Moreover the surface of the obtained grafted film was found to be smooth and homogen compared to those obtained with benzene. Highest degree of grafting obtained in isopropanol most likely due to the trommsdorff-type effect (12). Lower degree of grafting is obtained in benzene because of the presence of resonance stabilization effect of benzene ring, which acts as an energy transfer agent (11).



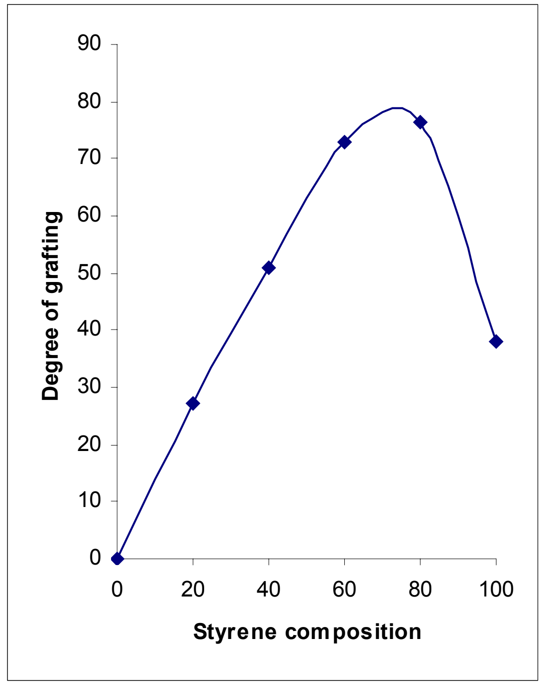


Fig. 1. Schematic diagram for the effect of different solvents on the degree of grafting of styrene onto ETFE films (50%v/v) at irradiation dose 100kGy.

Fig. 2. Schematic diagram for the effect of different solvents on the degree of grafting of styrene onto ETFE films (50%v/v) at irradiation dose 100kGy.

3.2. Effect of monomer composition

The effect of monomer composition on the graft copolymerization onto ETFE film was investigated (see Fig. 2). It is shown that the maximum degree of grafting is at around 60 to 80% which is the maximum trommsdorff-type effect occurred. The increase in the final degree of grafting with the increase in styrene concentration is owing to the increase in the number of styrene molecules that react with the free radicals. However at 100% monomer, the degree of grafting is lower as the absence of solvent reduces the degree of grafting. This is because the solvent influences during grafting reaction by swelling polymer substrate to facilitate accessibility and diffusion of monomer to the active site (12).

3.3. FTIR measurements

Fig. 3 shows typical FTIR spectra of ETFE-g-PS films having various degrees of grafting. The original ETFE film is used as a reference. The presence of polystyrene in the films is confirmed by the presence of additional peaks representing benzene ring feature such as the stretching vibration of =C-H for benzene ring at 3010-3100 cm^{-1}, the skeletal C=C in-plane stretching vibrations in the range of 1500 to 1600 cm^{-1} and out-of-plane C-H deformation band at 700cm^{-1}.

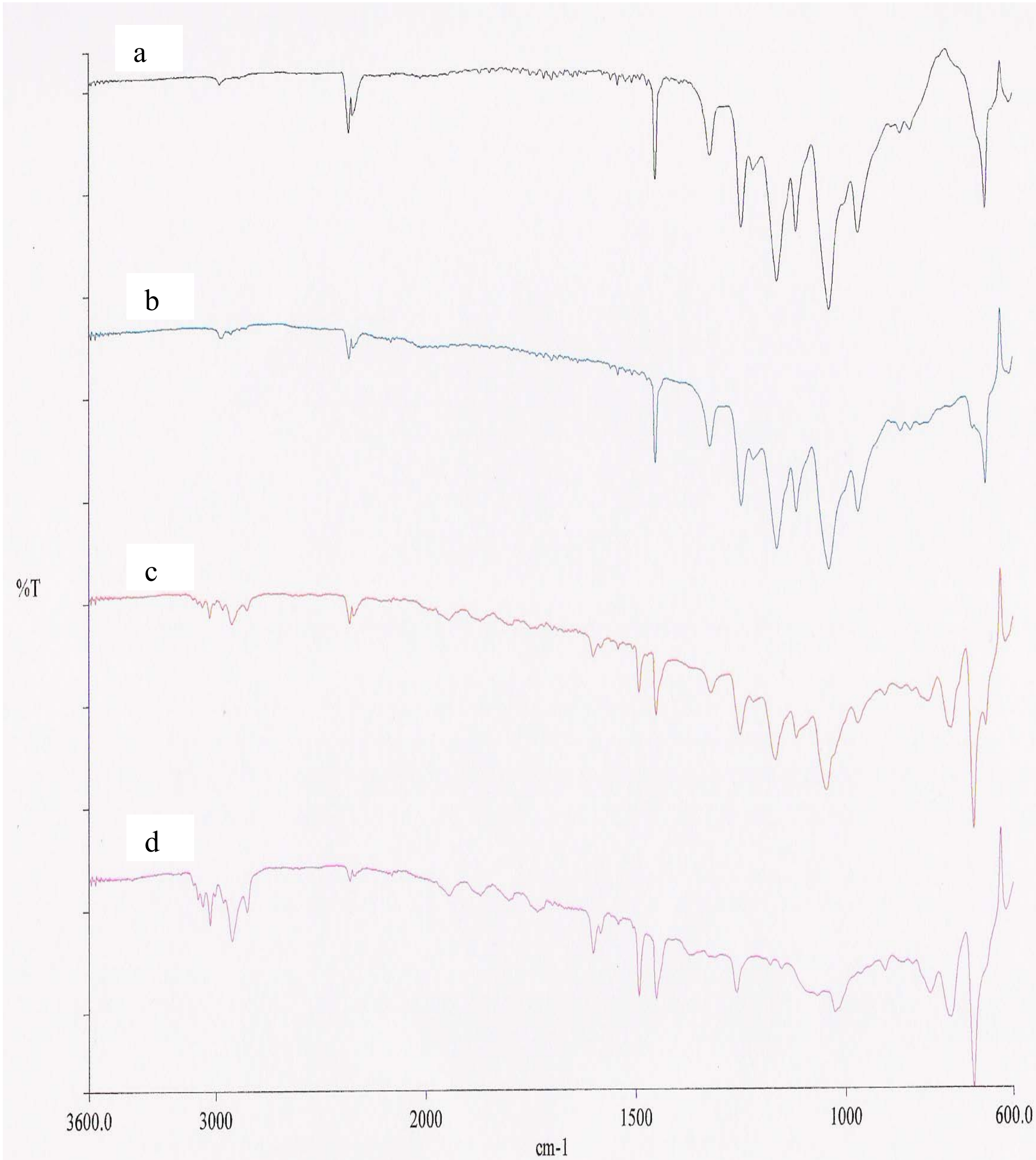


Fig. 3. FTIR spectra of original ETFE film (a), pre-irradiation grafted at 27% D.O.G (b), at 51% D.O.G (c) and at 73% D.O.G (d) ETFE films at 100kGy

4. Conclusion

Radiation grafted ETFE films were successfully prepared. Degree of grafting strongly dependent upon the monomer concentration of the grafting reaction. FTIR spectra confirmed the presence of styrene in the grafted films. Further work will be carried out to study the effect of other reaction parameter to obtain proton exchange membrane.

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