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Gamma-radiation-induced grafting of binary mixture of methacrylic acid and 4-vinyl pyridine onto Teflon-FEP film as an effective polar membrane for separation processes

Inderjeet Kaur [a], Sunita Rattan [b], Sandeep Chauhan [a], Nitika Gupta [a,*]

[a] Department of Chemistry, H.P. University, Shimla 171005, India
[b] Amity School of Engineering and Technology, New Delhi, India

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ABSTRACT

Ionic bifunctional membranes have been synthesized by grafting binary mixture of methacrylic acid (MAAc) and 4-vinyl pyridine (4-VP) onto Teflon-FEP film by pre-irradiation method. Optimum conditions pertaining to maximum percentage of grafting were evaluated as a function of different reaction parameters. Maximum percentage of grafting of binary mixture (MAAc-co-4-VP) (71.29%) was obtained at an optimum total dose of 54.48 kGy and the total concentration was 9.49 mol/L ([4-VP] = 0.07 mol/L and [MAAc] = 9.42 mol/L) in 5 ml of water. The effect of alcohols as additives to the reaction medium on percent grafting of the binary mixture has also been studied. The membranes were characterized by FTIR spectroscopy, scanning electron microscopy and thermogravimetric analysis. Swelling studies of the membranes were performed in different solvents such as water, benzene, carbon tetrachloride and dimethyl formamide (DMF). Maximum swelling was observed in DMF with minimum swelling in benzene. Metal ion (Cu^{2+}, Ni^{2+} and Fe^{2+}) uptake studies show better affinity for Fe^{2+} ions. Conductance measurements in different aqueous salt solution showed that these membranes have affinity for Na^+/K^+ ions and Cl^- ions and hence can be used in desalination/separation processes for the separation of both type of cationic and anionic ions.

1. Introduction

Various types of techniques have been developed in recent years to prepare ion-exchange membranes for various applications such as electro dialysis, waste water treatment, and fuel cell applications [1,2]. Radiation-induced graft-copolymerization provides an attractive method for modification of chemical and physical properties of polymeric material to prepare ion-exchange membrane with high quality and low cost. Many efforts have been devoted to develop ion-exchange membranes by radiation-induced grafting technique [3,4]. Ion-exchange membranes are a promising material for the removal of toxic metal ions and the recovery of valuable proteins in various fields, such as semiconductor and pharmaceutical industries [5].

Fluoropolymers are known as chemically inert materials with good high temperature resistance, so they are often the materials of choice for harsh chemical environments. Fluoropolymers, especially polytetrafluoroethylene (PTFE), have been widely studied with respect to grafting with various monomers. Hegazy et al. [6] and Burillo and Chapiro [7] have studied the radiation-induced graft-copolymerization of vinyl and acrylic monomers onto fluorinated matrix such as Teflon, Teflon-FEP (tetrafluoroethylene-co-hexafluoropropylene), polyvinylfluoride and polyvinylidine fluoride because of their excellent thermal, chemical and mechanical stability. Grafting of functional monomers such as acrylic acid (AAc) and methacrylic acid (MAAc) directly confers ionic (cationic) characters to the polymer backbone [8,9]. Grafting of AAc onto pre-irradiated Teflon-FEP film was investigated, and the reaction parameters dose, dose rate, monomer concentration and grafting temperature were examined [10]. Bozzi and Chapiro have synthesized perm-selective membranes by grafting acrylic acid into air-irradiated Teflon-FEP films [11]. Radiation-induced grafting of acrylic acid (AAc) and sodium styrene sulfonate onto high-density polyethylene membranes was investigated by the pre-irradiation method, and a cation-exchange membrane containing bifunctional groups was synthesized. The effects of grafting conditions such as monomer concentration, radiation dose and temperature on grafting yield were studied [12]. Grafting of vinyl monomers containing polar pendant groups such as –C=N of 4-vinyl pyridine (4-VP) and –C≡N of methacrylonitrile (MAN) has been carried onto Teflon-FEP [13]. Tefzel, a copolymer of ethylene and tetrafluoroethylene, has been modified by grafting acrylonitrile (AN) and methacrylonitrile (MAN) onto it by a pre-irradiation method in aqueous

* Corresponding author.
E-mail addresses: nitikaguptahpu@yahoo.co.in, ij_kaur@hotmail.com (N. Gupta).

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medium. The effect of aliphatic alcohols of varying chain length on percentage add-on of AN and MAN has also been studied [14]. Synthesis and characterization of polyethylene film radiochemically grafted with 4-VP and its use in water desalination [15,16,13] was successfully carried out by Kaur et al. Radiation-induced graft-copolymerization of styrene and AAc onto Teflon-FEP films was reported for proton exchange membranes [17]. Gamma-radiation-induced grafting of styrene onto Teflon-FEP films was investigated by the pre-irradiation method [18]. Radiation-induced graft-copolymerization of AN onto polypropylene and poly (TFE-co-ethylene) copolymer films has been studied [19]. Hegazy et al. [20] characterized the radiation grafted membranes and used these membranes for application in waste water treatment. The membranes based on polytetrafluoroethylene find extensive applications as separators in batteries, electro dialysis cells, and electrochemical systems [21] and in electrochemical devices and fuel cells [22]. Graft chains containing ion-exchange groups expand or shrink depending on the ionic strength, pH, and kind of solvent used [23,24]. There are abundant reports on grafting of single monomers onto fluorinated films to impart membrane properties to these films, but reports of grafting of binary mixture on these films are scanty. So, the present work is aimed to obtain bifunctional membrane with high selectivity by grafting of binary mixture of 4-VP and MAAc onto Teflon-FEP film by pre-irradiation method.

2. Experimental

2.1. Materials and methods

Teflon-FEP films (0.05 mm thickness) obtained from Dupont through the courtesy of Prof. A. Chapiro of CNRS Thiais, Paris, France, methacrylic acid (Merck) was used as received; while 4-vinyl pyridine (Acros) was distilled before use .Double distilled water was used as the reaction medium for graft-copolymerization.

2.2. Irradiation of Teflon-FEP Films with gamma-rays

Teflon-FEP film was cut into small strips of size (2 cm × 4 cm), washed with methanol, dried and weighed. Irradiation of Teflon-FEP film was carried out with gamma-rays from Co^{60} source, housed in 'Gamma chamber 900' (BARC, Mumbai) for different time periods at a constant dose rate (2.27 kGy/h).

2.3. Graft-copolymerization

The pre-irradiated and weighed Teflon-FEP film (2 cm × 4 cm) was placed in a standard joint two necked flask, fitted with water condenser and thermometer. To it was added a definite amount of water (5–35 ml), followed by the addition of a known amount of monomer [MAAc(0.1–11.7 mol/L/4-VP (0.03–3.7 mol/L))] taken in definite proportions. The reaction mixture was placed in an oil bath and refluxed for definite time period (60–210 min). After the reaction was over, the membranes were removed from the flask, washed with appropriate solvent system water and [acetone–water (1:1) mixture] to remove any homopolymer (poly(MAAc) and poly(4-VP) respectively) and copolymer (poly(MAAc-co-4-VP) formed during the reaction. The membranes free from homopolymer/copolymer were dried till constant weight was obtained. Percentage of grafting (P_g) was calculated from increase in weight of the original film as follows:

$$\text{Percentage of grafting } (P_g) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are the weights of pristine film and the grafted membrane respectively after the complete removal of the homopolymer/copolymer. Percentage of grafting has been determined as a function of total dose, amount of water, monomer concentration, reaction time and reaction temperature.

2.4. Characterization of grafted films: evidences of grafting

Grafting was established by following methods:

(i) Physical properties viz. (a) appearance (b) area.
(ii) FTIR spectroscopy: FTIR spectra of pristine Teflon-FEP and Teflon-FEP-*g*-poly(MAAc-co-4-VP) were obtained on Nicolet-5700 IR spectrophotometer.
(iii) Thermogravimetric analysis: TG analysis of pristine and the grafted film were carried out on Schimadzu DTG-60H Thermal Analyzer.
(iv) **S**canning electron microscopy: surface topology and homogeneity of Teflon-FEP film and grafted Teflon-FEP film i.e. Teflon-FEP-*g*-poly(MAAc-co-4-VP) was studied by scanning electron microscopy of model JEOL JSM 6100.
(v) Swelling studies: swelling behavior of Teflon-FEP-*g*-poly (MAAc-co-4-VP) membranes has been studied in solvents such as water, benzene, carbon tetrachloride and dimethyl formamide (DMF). Samples of Teflon-FEP-*g*-poly(MAAc-co-4-VP) of known weight were immersed separately in each solvent at 30 °**C** for different time period. After the specified time period, the membranes were removed from each solvent and dried between the folds of filter paper to remove the liquid adhering to the surface and weighed immediately. The percentage swelling (P_s) was calculated as:

$$\text{Percentage swelling } (P_s) = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of the swollen and dry films respectively.
(vi) Ion uptake studies: the main application of these membranes is in the ion uptake from the electrolytic solutions. In order to study the ionic behavior of Teflon-FEP-*g*-poly (4-VP-co-MAAc) membrane, the membranes were suspended separately in 0.5% and 1% aqueous solutions of NaCl, KCl, Na_2SO_4 and K_2SO_4 solutions for 24 and 48 h at 30 °C. After the stipulated time periods the membranes were removed from these solutions and the conductance of the residual salt solutions were measured and compared with the conductance of the respective reference salt solutions. To further validate the ion uptake by the membrane, the films, after the removal from the salt solution were pressed between the folds of the filter paper to remove the adhered salt solution and placed in the double distilled water for 24 and 48 h at 30 °C. The membranes were removed after the specified time and the conductance of the double distilled water was noted and compared with the conductance of the reference distilled water.
(vii) Metal ion uptake studies: in order to study the effect of the pendent polar groups of the grafted binary monomer mixture in affectively binding the metal ions, metal ion uptake studies have been carried out specifically for Cu^{2+}, Ni^{2+}, and Fe^{2+} ions. The binary monomer grafted Teflon-FEP membranes were taken and immersed in aqueous solutions of 0.1 M $CuSO_4$ and 0.1 M $NiSO_4$ for different time periods (4, 8 and 24 h) and in 0.1 M $FeSO_4$ solution for 1 and 2 h. After the stipulated time period the films were removed from the salt solutions. Filtrates of residual solutions were analyzed for concentration of rejected ions on UV–vis spectro-