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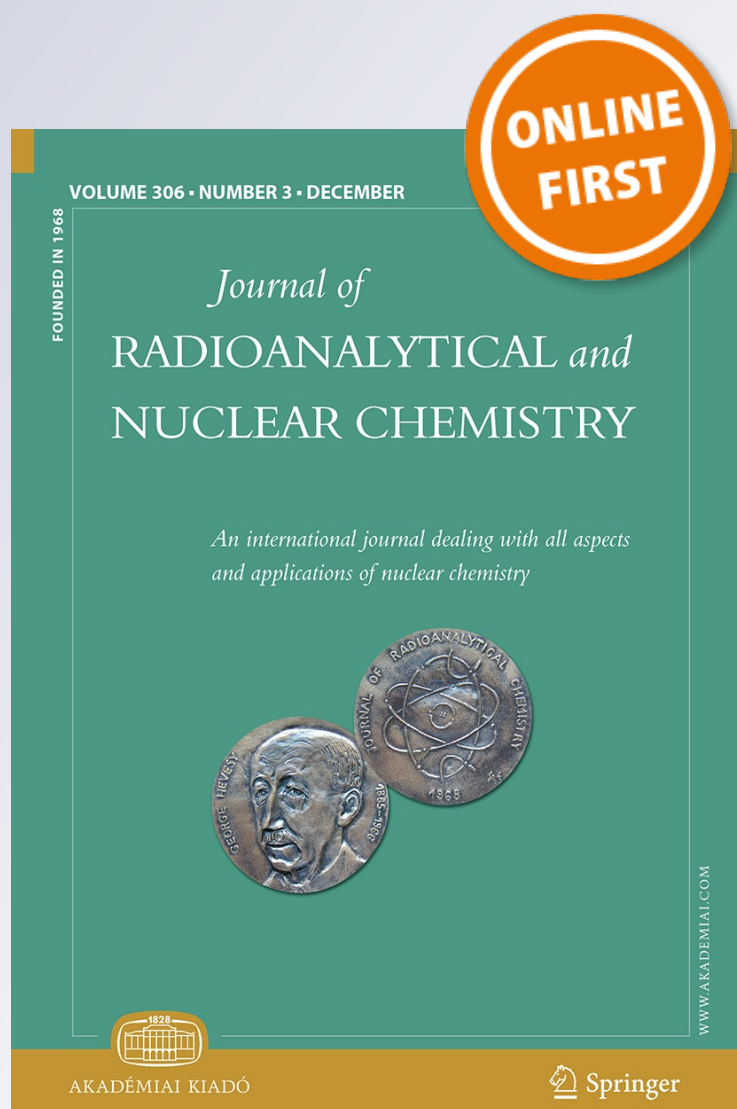
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Grafting of nitrogen containing monomers onto poly(ethylene-alt-tetrafluoroethylene) films by bulk polymerization for proton exchange membranes

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Abstract Bulk polymerization is suggested as an alternative to solution polymerization to graft N-containing monomers onto poly(ethylene-alt-tetrafluoroethylene) films to produce highly conductive membranes. Among the tested monomers, 4-vinyl pyridine was found as the most reactive monomer giving grafting levels (%GL) >120 % compared with %GL <45 % previously reported under similar conditions. Doping grafted films with H₃PO₄ converted them to membranes with enhanced water swellability but their conductivity values were at the same order of magnitude of membranes prepared by solution polymerization. These results demonstrate the importance of having both high grafting levels and homogeneous distribution of grafting throughout the base polymer.

Keywords Radiation induced grafting · Bulk polymerization · N-containing monomers · ETFE films

Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are considered to be among the most attractive and promising sources of electrical power. Potential applications of PEMFC are stationary power stations, automobile engines and portable electronics [1, 2]. Perfluorinated polymers

such as Nafion are widely used in PEMFC because of their superior chemical and electrochemical stability and high proton conductivity. But these membranes have two shortcomings: a reduced conductivity at elevated temperatures or in low humidity, and high preparation costs [3]. To circumvent these disadvantages, much effort has been expended in developing new membranes. Of various alternatives, radiation graft polymerization is employed to develop cost-effective and highly conductive membranes [4].

Radiation-induced grafting is a commonly used method for the modification of surface and bulk properties of polymeric materials. Advantages of this process include: simplicity, low costs, control over process, and adjustment of the materials composition and structure [5–7]. Grafting can be performed using two methods: irradiation of the base polymer in the presence of a monomer (simultaneous radiation grafting) or without a monomer (pre-irradiation grafting). Because monomers are not exposed to radiation in the pre-irradiation technique, homopolymer formation rarely occurs as it does in the first simultaneous technique [5].

High performance PEM were prepared by radiation-induced grafting of a monomer or mixture of monomers onto hydrophobic film, which acts as the base polymer. Styrene was grafted onto hydrocarbon polymers; the subsequent sulfonation of grafted chains converted them to PEM [8]. Schmidt et al. reported alternative acid-base composite membranes by grafting N-containing monomers onto ETFE films pre-irradiated with electron beam prior to their doping with PA [9]. Among these monomers, 4VP dissolved in tetrahydrofuran gave a limiting grafting level of nearly 50 % after about 1 h. Şanlı et al. reported preparation of PEM by grafting 4VP, 2VP and NVP from their solutions onto ETFE films pre-irradiated with γ -ray followed by doping with PA [10, 11]. They found a

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correlation between proton conductivities of the produced membranes with grafting levels. Membranes prepared by grafting 4VP gave best results, as grafting uptake of 45 % could be obtained after 4 h. Increasing grafting levels by elongation of reaction time failed as a drop in grafting uptake was noted with all reacted monomers beyond 4 h. Nasef et al. reported grafting 4VP dissolved in tetrahydrofurane onto ETFE films irradiated by electron beam and doped with PA. Grafting uptake showed a drastic increase in the first hour before leveling off to less than 50 % beyond a 4 h reaction time [12]. Proton conductivities of the produced membranes were found to be dependent on the degree of grafting as more N- sites are available for loading phosphoric acid (PA). Kinetic behavior and optimization of the radiation-induced grafting of 4VP onto ETFE were investigated in two recent studies [13, 14]. The reported optimum reaction conditions were 4 h at 60 °C at monomer concentration of 50 % while the optimum grafting uptake was found to be around 60 %.

In this work, bulk polymerization is proposed as an alternative to solution polymerization to graft 4VP, 2VP, and NVP onto ETFE films pre-irradiated with γ -ray. To my knowledge, this is the *first article reporting* the use of *bulk polymerization* to graft ETFE films with these monomers prior to doping with PA. To make a fair comparison between the two polymerization techniques, grafting by bulk polymerization will also be carried out under the same optimum conditions reported in previous works. Bulk polymerization is expected to give grafting levels *not achievable* by solution polymerization due to the availability of high concentrations of monomers, in addition to the elimination of possible transfer reactions to solvents. High degree of grafting is expected to enhance acid uptake and water swelling of the obtained membranes. The ability of PEM to swell water is one of several important factors that contributes to their effectiveness as proton conductors [1, 15]. A schematic representation of grafting and doping processes is shown in Fig. 1.

Experimental

The base polymer poly(ethylene-alt-tetrafluoroethylene), or ETFE, was purchased in the form of a 25 μm thick film (Nowoflon ET-6235) from Nowoflon GmbH (Siegsdorf,

Germany). The monomers (4VP, 2VP, and NVP), the solvents and PA were supplied by Sigma Aldrich and used without further purification. The ETFE base polymer was cut into 8 \times 8 cm films, washed with ethanol, and dried in a vacuum oven at 80 °C for 1 h. The dried films were placed one-by-one in polyethylene zip-lock bags to prevent contamination. Irradiation of the films was performed at γ -Pak Sterilization (Çerkezköy, Turkey) using gamma rays from a ^{60}Co source. The irradiation was carried out in air at room temperature with doses of 10 and 50 kGy. After exposure, the films were stored at -80 °C until used. For the grafting process, irradiated films were placed into glass tube reactors; grafting monomers were added to these reactors and then purged with dry nitrogen for 30 min. The reactors were subsequently sealed and placed in thermostated water bath at 60 °C. Six samples were prepared and reacted with each monomer at a given absorbed dose. At the end of reaction time, the grafted films were washed with *n*-butanol to remove residual monomer and/or polymer, which were not bonded to the base film, dried at 70 °C and reweighed. The percentage of graft level (% GL) is calculated as follows:

$$\% \text{ GL} = \frac{w_g - w_i}{w_i} \times 100$$

where w_i and w_g are the weights of the film before and after grafting, respectively.

The grafted films were doped with PA by immersion in 14 M acid solution at 60 °C for 20 h. Doped films were then washed several times with copious amounts of distilled water and dried at 70 °C until constant weight was reached. The percentage of doped level (% DL) is calculated as follows:

$$\% \text{ DL} = \frac{w_d - w_g}{w_g} \times 100$$

where w_g and w_d are the weights of the grafted copolymer before and after doping, respectively. To determine water uptake, the obtained membranes were placed in deionized water at room temperature for 24 h, until the water absorption equilibrium was reached. Then the membranes were removed, placed on filter paper to remove excess surface water, and weighed. Water uptake is calculated using the following equation:

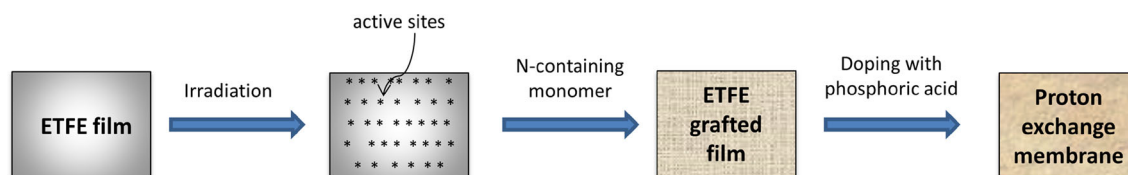


Fig. 1 Schematic representation of proton exchange membrane synthesis

$$\% \text{ Water uptake} = \frac{w_w - w_d}{w_d} \times 100$$

where w_w and w_d are weights of the wet and dry (doped) membrane, respectively. Each experiment was repeated three times.

Proton conductivity was measured by Gamry PC14 Potentiostat with BT-1005 BektTech Scanning DC Software in 100 % of relative humidity at ambient temperature according to four point probe technique.

Results and discussion

Grafted ETFE films were abbreviated ETFE-g-P4VP, ETFE-g-PNVP, and ETFE-g-P2VP, respectively. To compare bulk polymerization and the results of solution polymerization, all grafting processes were carried out under optimum reaction conditions reported in previous works. The results of grafting ETFE pre-irradiated films at 10 and 50 kGy are shown in Figs. 2 and 3. 4VP was found to be the most reactive monomer as GL in the range of 100–160 % was observed. These values are *two to three times* the previously reported values from solution polymerization [10–14]. The reactivity of 4VP was pronounced enough to induced changes in the dimensions of grafted films (increase in thickness and area); these films became rigid and fragile with wrinkles in their appearance. High GL occurs because bulk polymerization has the advantage of supplying active sites at the irradiated films with high concentrations of monomers and prevents possible transfer reactions to solvent.

The influence of the nature of reacting monomers and absorbed dose on average GL values is shown in Fig. 3. 4VP which was found to be much more reactive than 2VP and NVP in solution polymerization showed similar tendency in bulk polymerization. Monomer reactivity during

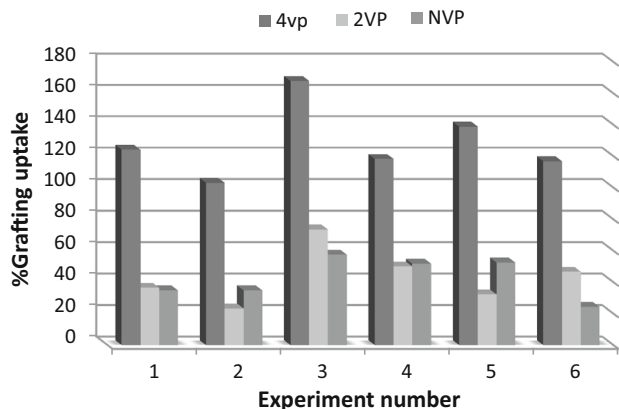


Fig. 2 The % grafting uptake of 4VP, 2VP and NVP onto ETEF base polymer at irradiation dose of 50 KGy

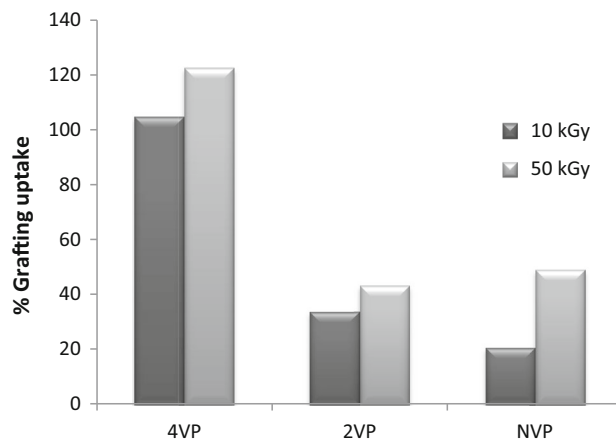


Fig. 3 Average % Grafting uptake levels of bulk polymerization of 4VP, 2VP and NVP onto ETFE films at absorbed doses of 10 and 50 kGy

grafting is one of the main important factors that control GLs. This reactivity depends upon various variables, such as polarity, steric factor and the ability of the monomer to be swelled on the backbone of the base polymer [6]. The difference in reactivities of 4VP and 2VP that have similar structures and polarities may be attributed to steric factor, which acts in favor of 4VP. The increase in GLs with increasing absorbed dose is an expected result as more radicals are formed into ETFE films exposed to 50 kGy irradiation compared with that at 10 kGy.

To convert grafted films to PEM, two samples were treated with PA and the average DLs are shown in Fig. 4. Weight gain was observed in all samples except one ETFE-g-P2VP sample in which doping ended up with weight loss as shown in Table 1. This finding is partially consistent with the results reported by Sanlı et al. who noted weight gain after doping ETFE films grafted with 4VP while

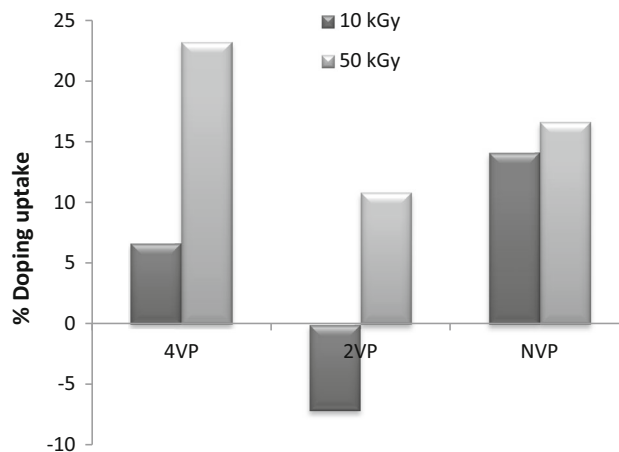


Fig. 4 The % doping uptake of phosphoric acid onto ETFE-g-P4VP, ETFE-g-PNVP and ETFE-g-P2VP grafted films

doping films grafted with 2VP and NVP ended up with mass loss [11]. This mass loss was attributed to degradation and leaching out of unbounded material from the membrane matrix during the doping process, which requires the immersion of grafted films in concentrated PA at 60 °C for 20 h. Due to this mass loss, it was difficult to find a correlation between GLs and DLs for all grafted films.

The availability of hydrophilic groups onto the produced membranes at the end of grafting and doping can be deduced from the values of water uptake levels. Conversion of the hydrophobic ETFE polymer, which has no affinity to water, to hydrophilic matrix is the result of grafting and doping processes. This affinity to water is the result of intermolecular hydrogen bonding between water and both N–H groups and PA of the produced membranes. As shown in Fig. 5 the highest water uptake levels were observed with ETFE-g-P4VP membranes reaching about 60 % which is about 2 folds the value obtained in previous work [11]. Contrary to the findings of Sanlı et al. which reported higher water affinity of NVP grafted films compared with films grafted with 2VP, the results of this work revealed higher water swelling for ETFE-g-P2VP membranes [11]. These water uptake values were in the range between 10 and 20 % for ETFE-g-P2VP while for ETFE-g-PNVP membranes these values were less than 8 %.

Proton conductivity is critical for operational PEMs and is often the first characteristic considered when the practicability of newly-developed membranes is evaluated for fuel cell applications [16]. Proton conductivity of the membranes prepared in this work is expected to be similar to that of poly(benzimidazole) (PBI) doped with PA, which has been extensively studied. The major contribution to proton conductivity is expected to come from proton hopping from N–H site to phosphoric acid anion (Grotthus diffusion mechanism). Additionally, proton hopping via water molecules explains the improvement in proton conductivity with an increase in atmospheric humidity [17, 18]. Consequently, the increase in GLs as a result of bulk polymerization was expected to contribute positively to proton conductivity of the produced membranes. As GL increases, more –N– sites will be available for proton

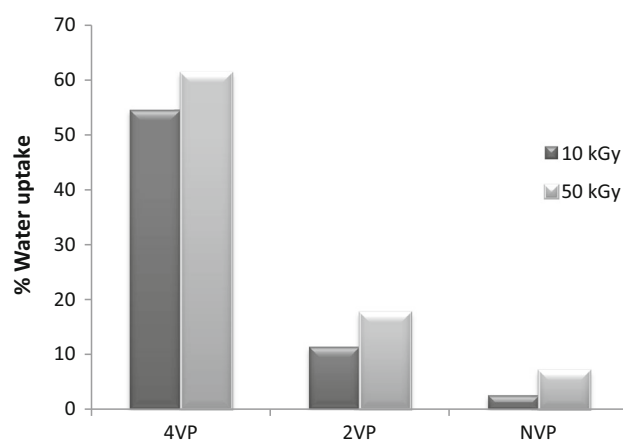


Fig. 5 The % water uptake of ETFE-g-P4VP, ETFE-g-PNVP, and ETFE-g-P2VP membranes

hopping and for PA loading in addition to the enhancement of water swelling. Proton conductivities of selected PEM samples in addition to GL, DL and water uptake values are given in Table 1. Reliable and stable proton conductivity measurements were obtained only with ETFE-g-P4VP membranes. All ETFE-g-PNVP and ETFE-g-P2VP membranes did not show any proton conductivity with one exception of an ETFE-g-P2VP sample.

Proton conductivity values of ETFE-g-P4VP membrane were in the range between 33 and 35 mS/cm at room temperature and 100 % humidity. These values are of the same magnitude of the reported values by Sanlı et al. although they reported much lower grafting and water uptake levels [11]. The performance of ETFE-g-P4VP membrane prepared in this work did not meet the expectation of improving proton conductivity as a consequence of increasing grafting and water uptake levels. This may be related to heterogeneous distribution of grafting along the cross-section of grafted films due to absence of solvent. According to grafting front mechanism, grafting starts at the surface fronts of the base film and moves toward the interior [19]. Solvents in radiation grafting enhance the accessibility of monomer to the grafting sites due to the ability of these solvents to swell the base polymer. In good

Table 1 Graft levels, doping levels, water uptake and conductivity of selected ETFE films grafted with bulk polymerization

Monomer	Absorbed dose (kGy)	% Graft level	% Doping level	% Water uptake	Conductivity (mS/cm)
4VP	10	104.4	3.0	51.0	33
	50	116.8	35.6	61.7	35
2VP	10	44.8	–6.6	11.5	–
	50	46.7	9.7	21.2	38*
NVP	10	24.3	13.7	3.4	–
	50	34.8	14.5	4.7	–

* Moderately stable measurement

solvents grafting across the film thickness is highly favored to give homogeneous grafting while in poor swelling solvents, surface grafting occurs due to the slowing down of monomer diffusion within the base polymer [6, 20]. By employing bulk polymerization and due to the absence of solvent and to the increase in the viscosity of the polymerization mixture the diffusion of monomer molecules to the radical sites is expected to be hindered which leads to surface grafting. [9]. No proton conductivities could be detected for all ETFE-g-P2VP and ETFE-g-PNVP membranes with one exception as one ETFE-g-P2VP gave a fairly stable conductivity. The same sample showed the highest grafting and water uptake levels. These results are different from previous work as they reported low proton conductivity values for ETFE-g-PNVP samples while ETFE-g-P2VP found to be not conducting [11].

Finally, it should be emphasized that the results presented in this work are preliminary in nature. A thorough investigation of using bulk polymerization as an alternative to solution polymerization for grafting processes is required. Such investigation should try first to find out the *optimum conditions* of grafting reactions in addition to evaluation of the effects of grafting process on *mechanical* and *thermal* properties and *morphological characteristics* of the grafted films.

Conclusion

Bulk polymerization was used to graft three nitrogen containing monomers (4VP, 2VP and NVP) onto poly(ethylene-alt-tetrafluoroethylene) (ETFE) films pre-irradiated with γ -ray followed by doping with PA to produce PEM. Among the monomers tested, 4VP was found to be the most reactive with grafting uptake in the range of 100–160 % which is two to three folds the values obtained by grafting from solution polymerization. Doping ETFE-g-P4VP with H_3PO_4 converted them to PEMs that showed high water swellability but their proton conductivities were in the same magnitude of those membranes produced by solution polymerization. The use of bulk polymerization technique was accompanied by an increase in grafting uptake but, due to the absence of solvent, the grafting is expected to be heterogeneous, which may explain the unexpected low proton conductivity of the obtained membranes.

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