Preparation and Characterization of Phosphoric Acid Composite Membrane by Radiation Induced Grafting of 4-Vinylpyridine onto Poly(ethylene-co-tetrafluoroethylene) Followed by Phosphoric Acid Doping

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ABSTRACT: Preparation of phosphoric acid composite membranes by radiation induced grafting of 4-vinylpyridine (4-VP) onto electron beam irradiated poly(ethylene-co-tetrafluoroethylene) film followed by phosphoric acid doping was investigated. The effect of grafting parameters (monomer concentration, absorbed dose, reaction time, and temperature) on the degree of grafting ($G\%$) in the membrane precursor and its relation with the amount of acid doped was studied. The proton conductivity of the obtained membranes was evaluated in correlation with $G\%$ and temperature using ac impedance. Fourier transform infrared, thermal gravimetric analysis, X-ray diffraction, and universal mechanical tester were used to investigate chemical composition, thermal resistance, structure, and mechanical properties of the membranes, respectively. The membranes of 34 and 49% recorded high proton conductivity in the magnitude of 10^{-2} S cm^{-1} without humidification. The membranes were also found to have reasonable mechanical integrity together with thermal stability up to 160°C. The obtained membranes are suggested to be less-water dependent and have potential for testing in high temperature polymer electrolyte membrane fuel cell. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polymer electrolyte membranes (PEM) play a crucial role in the electricity generation in PEM fuel cells. Such role includes separation of the anode from the cathode to prevent the bulk mixing of H$_2$ and O$_2$ while selectively transporting H$^+$ (protons) between the two electrodes. Thus, the search for a new alternative and cost effective proton conducting membranes for PEM fuel cell continues to attract a significant attention in the field of advanced materials and electrochemical systems.[1] Recently, radiation induced grafting (RIG) has emerged as an attractive method for preparation of sulfonic acid PEM.[2] This is due to its versatility and ability to introduce the hydrophilic functional groups to preformed hydrophobic polymer films in a way overcoming the difficulty of shaping the ionic membranes.[3] The availability of various monomers and polymer films combinations provide chances for obtaining high quality membranes with desired compositions and properties for specific applications.[4] Preparation of PEM bearing sulfonic acid for fuel cell by

RIG has been a frequent topic recently reviewed in the literature.[4,5] However, proton transport in the sulfonic acid bearing membranes such as Nafion, their commercial analogs and the newly developed radiation grafted counterparts takes place in the aqueous phase of these membranes and therefore, it is necessary to have an adequate humidification during PEM fuel cell operation. The presence of excess or less water in the membranes hinders the performance of PEM fuel cell. Thus, the usage of such membranes was limited to PEM fuel cell operating at 60-80°C.[6,7]

To enhance PEM performance, the technology has to move toward higher temperature operation to increase the efficiency and reduce the dependency on water and its associated management problem. This can be achieved by developing an alternative PEM bearing other functional groups that can withstand temperatures above 100°C. Acid/base complexed membrane obtained by radiation induced grafting of polar heterocyclic monomers such as 4-vinylpyridine (4-VP) onto poly(ethylene-co-

Table I. Summary of Previous Studies on Preparation of Radiation-Grafted PEMs Based on ETFE Films

Base polymer/ thickness (µm)	Monomer system	Radiation source/method	Functional group	Refs
ETFE/50	4-VP[a];1-VIm[b]	EB(1MeV)/preirradiation(in air)	Phosphoric acid	8
ETFE/ 125	Styrene	γ-radiation/preirradiation(in N_2 atmosphere)	Sulfonic acid	9
ETFE/125	Styrene/DVB[c]	γ-radiation (60Co)/simultaneous irradiation (in N_2 atmosphere)	Sulfonic acid	10
ETFE/100	Styrene/DVB	EB(1.5MeV)/preirradiation (in air)	Sulfonic acid	11
ETFE/25	Styrene /DVB	EB/preirradiation	Sulfonic acid	12
ETFE/25	4-VP; 2-VP[d]	γ-radiation (60Co)/preirradiation(in air)	Not available	13
ETFE/50	MeSt[e]/tBuSt[f]/DVB/BVPE[g]	γ-radiation (60Co)/preirradiation (in argon gas)	Sulfonic acid	14,15
ETFE/35	No monomer	Proton radiation	Sulfonic acid	16
ETFE/variable	Styrene/DVB	γ-radiation (60Co)/preirradiation(in air)	Sulfonic acid	17
ETFE/50	VBC[h]/AN[i]	β- radiation/ preirradiation(in N_2 atmosphere)	Triethylphosphite	18

[a]4-VP, 4-vinylpyridine. [b]1-VIm, 1-vinylimidazole. [c]DVB, divinylbenzene. [d]2-VP, 2-vinylpyridine. [e]MeSt, m, p-methylstyrene. [f]tBuSt, p-tert-butylstyrene. [g]BVPE, bis(p, p-vinyl phenyl) ethane. [h]VBC, vinylbenzyl chloride. [i]AN, acrylonitrile.

tetraflouroethene) (ETFE) film followed by doping with phosphoric acid was attempted as a PEM for proton conduction in high temperature PEM fuel cells.[8] The 4-VP was selected to provide a basic center ($-N^+$-) that conducts protons at temperatures above 100°C when doped with phosphoric acid (PA). On the other hand, the selection of ETFE film as a base polymer in this work and previous studies[9–18] related radiation grafted PEM with various functional groups summarized in Table I is due to its chemical inertness, thermal stability, and mechanical integrity in addition to high radiation resistance.[19] However, details of effects of grafting parameters such as monomer concentration, absorbed dose, and temperature on the degree of grafting during preparation of the membrane precursor in Ref. 8 were not reported. In another study, grafting of 4-VP onto ETFE film using preirradiation grafting method with γ-rays in the air was investigated with attention mainly paid to the role of solvent.[13] However, there was no mentioning of details of the grafting conditions and the doping procedure for the obtained membrane precursor with phosphoric acid.

The objective of this study is to report a complete investigation on the preparation of grafted membrane precursor of a basic nature by radiation induced grafting of 4-VP onto electron beam (EB) irradiated ETFE films under controlled conditions and its conversion to composite acid/base PEM by doping with PA. The physical and chemical properties of the membranes were evaluated in correlation with PEM fuel cell requirements using various analytical and material research aspects.

EXPERIMENTAL

Materials
ETFE films with a thickness of 125 µm was obtained from Nowofol GmbH (Siegsdrof, Germany) and used as polymer substrates for preparation of the membrane. Pieces of ETFE film of surface area 25 cm[2] were used as standard samples. 4-VP of purity more than 95% (Aldrich, Milwaukee, WI) was used immediately after purification by vacuum distillation under reduced pressure (6.7 mbar, 54°C). 85% phosphoric acid (JT Bakers,

Center Valley, PA) and deionized water produced using water purifier (NANOpure® DIamond™, Lake Balboa, Ca) were also used. Other solvents such as ethanol, tetrahydrofuran, and methanol were research grade and used as received.

Preparation of the Membranes
Membrane Preparation. The membrane preparation was performed in three-step procedure including irradiation of ETFE film, grafting of 4-VP, and acid doping. First, the ETFE film was irradiated with EB (NHV-Nissin high voltage, EPS 3000, Cockroft Walton type, Japan) to the desired dose under vacuum after being cleaned up with ethanol followed by vacuum drying. The samples were kept in a low temperature freezer at -65°C prior to use.

The grafting of 4-VP onto ETFE film was performed by placing an irradiated film in a glass ampoule that was tightly sealed and evacuated to remove air. A N_2-bubbled monomer solution composes of 4-VP and diluted with tetrahydrofuran to desired concentration was introduced through a special connection and the ampoule was sealed. The ampoule containing the film and monomer solution was placed in a water bath of selected temperature and the reaction was carried at desired time. Details of EB operating conditions together with irradiation and grafting parameters are given in Table II.

The grafted film was removed and extracted with methanol and tetrahydrofuran in a vessel under sonication for several hours to remove the unreacted monomers and homopolymer. The grafted film was dried under vacuum and the degree of grafting (G%) was calculated as follows:

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

where, W_o and W_g are the weights of original and grafted ETFE films, respectively.

The grafted films were doped with PA using a procedure reported by Li et al.[20] The grafted films were immersed in 85%

Table II. Parameters of EB Accelerator and Irradiation Conditions of ETFE Films

EB acceleration parameters:	
Accelerating voltage	500 keV (ETFE)
Beam current	2.0 mA
Dose per pass	10 kGy
Irradiation conditions:	
Atmosphere	Vacuum
Temperature	Ambient
Grafting conditions:	
Atmosphere	N_2
Absorbed dose (kGy)	20–100
Monomer concentration (vol %)	0–50
Reaction time (h)	0.25–6.0
Reaction temperature (°C)	30–70

aqueous PA for various periods of time at room temperature. The weight gain due to both water and PA was obtained by comparing the weight changes before and after doping. The acid doped membranes were dried at 110°C under vacuum until no weight change was reached to eliminate free water. The acid doping was estimated using eq. (2):

$$\text{Acid doping}\left(\frac{\text{mol of PA}}{\text{Poly(4VP) unit}}\right) = \frac{W_f - W_9}{W_9} \times \frac{\text{MW of 4VP}}{\text{MW of PA}}. \quad (2)$$

where, W_f and W_g are the weights of final PA doped membrane and grafted film, respectively. The molecular weight of 4-VP is 105 and that of PA is 98 g mol^{-1}.

Characterization of the Membranes

Fourier transform infrared (FTIR) measurements were carried out using a Nicolet (Magna-IR 560, Madison, WI) spectrometer equipped with attenuated total reflection, (Thunder dome-HATR) having *Ge* spherical crystal. The spectra were measured in a transmittance mode in a frequency range of 4000–500 cm^{-1}.

X-ray diffraction (XRD) measurements were performed using a Philips, Almelo, Netherlands, PW 1840, X-ray diffractometer. The diffractograms were collected at ambient temperature in a scanning range of 2θ 5–50° by means of Cu-Kα radiation (λ = 1.54Å) and monochromated by means of a Nickel filter.

Thermal gravimetric analysis (TGA) analysis of the membranes was performed using a Perkin-Elmer, Santa Clara, CA TGA-7. All the heating runs were made in a temperature range of 50–700°C at a constant heating rate of 20°C min^{-1} and under N_2 atmosphere.

The mechanical properties were performed on 50% humidified dumbbell-shaped specimens (50 mm long with a neck of 28 and 4 mm wide) according to ASTM D882. The measurements of tensile strength and elongation % at break were recorded on a universal mechanical tester (Instron, High Wycombe, England) at room temperature. The crosshead speed was fixed at 50 mm min^{-1}. A minimum of five specimens was tested for each sample. The data reported is an average of three readings.

Ionic conductivity of the membranes was measured at different temperatures (30–130°C) by a complex AC impedance spectroscopy. Measurements were carried on dried membrane samples using frequency response analyzer (Autolab PGSTAT 30, Eco Chemie, Netherland) at frequency range of 0.01–100 kHz. Circular samples were sandwiched between two stainless steel electrodes having round-end discs (20 mm diameter) hosted into self-made Teflon cell placed in an oven equipped with thermocouples and temperature controller. The ionic (proton) conductivity of PEM was calculated by taking the resistance obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance and membrane thickness into consideration.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

Figure 1 shows the relationship between the monomer concentration and G% for grafting of 4-VP onto ETFE films. As can be seen, G% increases gradually with the increase in the monomer concentration within the investigated range. This behavior can be attributed to the enhancement in the diffusion of the monomer to the grafting sites, which leads to the availability of more 4-VP molecules contributing to grafting reaction. This finding agrees well with that obtained earlier for similar grafting system (4-VP/ETFE).[20] Similar behavior was also observed upon grafting of other monomers such as styrene[21] and vinylbenzyl chloride (VBC)[18] onto ETFE films.

Effect of Absorbed Dose

Figure 2 shows the effect of the absorbed dose on the G% for grafting of 4-VP onto ETFE films. G% was found to increase steeply with the increase in the irradiation dose. This behavior can be attributed to the increase in the amount of radicals formed in the ETFE film and the increase in their involvement in the grafting reaction with the increase in the absorbed dose. These results suggest that the G% in the present system is a function of the amount of radicals formed in the polymer films and the concentration of the monomer in the grafting sites.
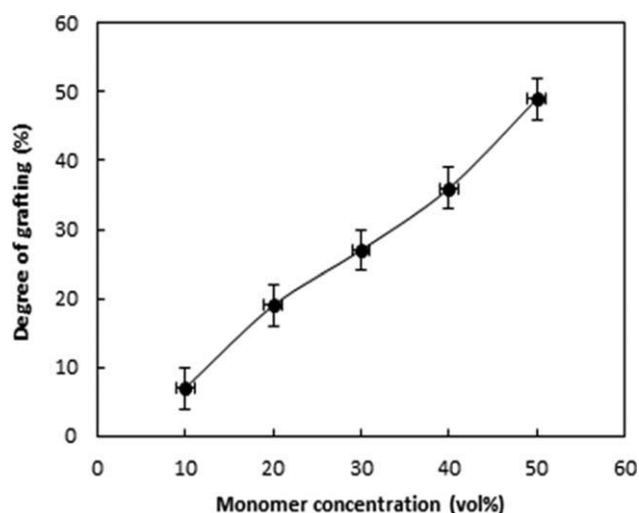

Figure 1. Degree of grafting vs. monomer concentration for grafting of 4-VP onto ETFE films. Grafting conditions are: absorbed dose, 100 kGy; reaction time 6 h; and temperature, 60°C.
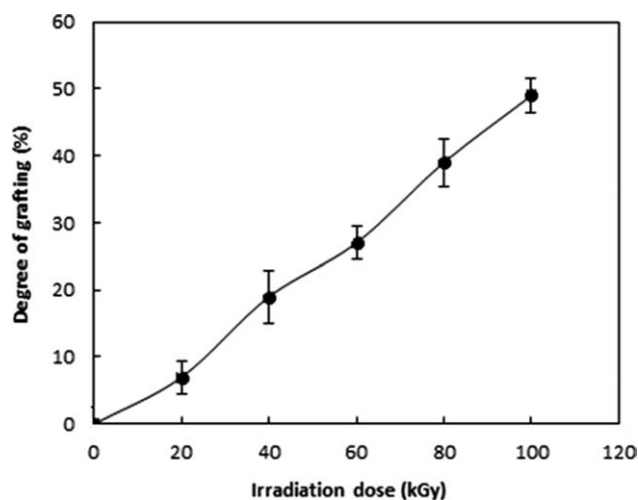
Figure 2. Variation of the degree of grafting with irradiation dose for grafting of 4-VP onto ETFE films. Grafting conditions are: 4-VP concentration, 50 vol %; reaction time 6 h; and temperature, 60°C.

Effect of Reaction Time

Figure 3 shows the variation of G% for grafting of 4-VP onto ETFE film with the reaction time. As can be seen, G% drastically increases in the first hour suggesting a high initial grafting rate followed by a small but obvious increase in G% up to 4 h, beyond which it tends to level off. The highest G% was achieved at 6 h and thus it is used as constant reaction time in the rest of the experiments. This behavior can be attributed to the initial enhancement of the diffusion of 4-VP to the grafting sites which leads to availability and involvement of more monomer molecules in the grafting reaction. As reaction time increases from 1 to 4 h and above, the viscosity of the grafting zone tends to increase as a result of a side homopolymerization reaction between some monomer molecules leading to a reduction in the monomer diffusion and eventually achieving grafting saturation at 6 h. Similar trends was obtained for grafting of other
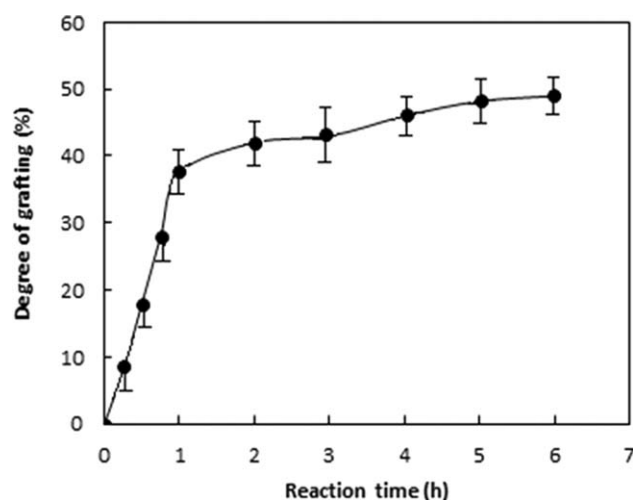

Figure 3. Variation of the degree of grafting with the reaction time for grafting of 4-VP onto ETFE films. Grafting conditions are: 4-VP concentration, 50 vol %; absorbed dose, 100 kGy; and temperature, 60°C.
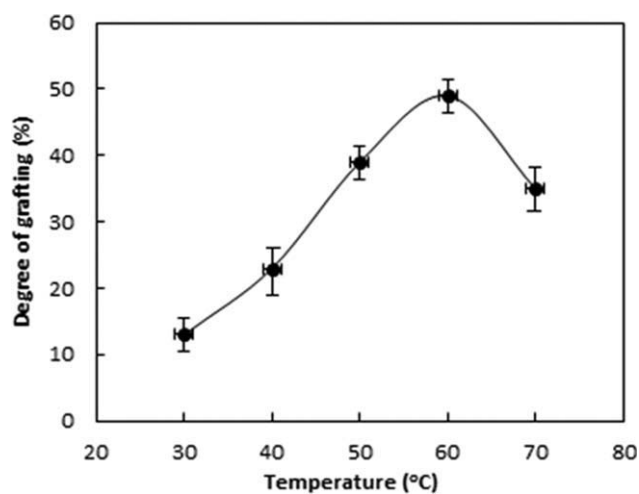

Figure 4. Variation of the degree of grafting with the temperature for grafting of 4-VP onto ETFE films. Grafting conditions are: 4-VP concentration, 50 vol %; absorbed dose, 100 kGy; and reaction time, 6 h.

monomers such as styrene,[21] p-styryltrimethoxysilane[22] and acrylic acid23 onto ETFE films.

Effect of Temperature

Figure 4 shows the variation of G% with the reaction temperature for grafting of 4-VP onto ETFE film. G% was found to increase with the increase in the temperature and achieved a maximum value at 60°C, beyond which it was dropped. The drastic increase in G% up to 60°C can be attributed to the increase in the reactivity of the thermally decomposed trapped radicals with the rise in temperature. This is mostly accompanied by an enhancement in the monomer diffusion and its availability in the grafting sites leading to an enhancement in the initiation and propagation rates couple with a delay in the termination. The decrease in G% at 70°C is likely to be caused by the mutual recombination of the trapped radicals taking place before reacting with the diffused monomer molecules and the bimolecular termination of the graft growing chains enhanced at higher temperatures. The heat effect in this study is similar to that for grafting of styrene[21] and acrylic acid[23] onto ETFE films.

Phosphoric Acid Doping

Figure 5 shows the variation of phosphoric acid doping with time for membranes having two different G% at room temperature. As can be seen, the number moles of PA per poly(4-VP) unit increases steeply in the first 30 h after which it tends to slow down and achieve a plateau after 40 h. The mole of PA/P4-VP unit increases with the increase in G% from 34 to 49%. These results suggest that the grafted films swell in the dopant solution facilitating the complexion of PA with –N- of the pyridine ring of poly(4-VP). The reaction seems to progressively proceed from the film surfaces toward the core through a sequence of diffusions of the acid molecules through the grafted layers until most of the available pyridine rings are fully occupied. Furthermore the increase in G% provides more pyridine rings for reaction leading to more acid/base complex centers. Similar behavior was reported for PA membrane based on radiation grafted precursor of ETFE films containing poly(vinylimidazole).[8]
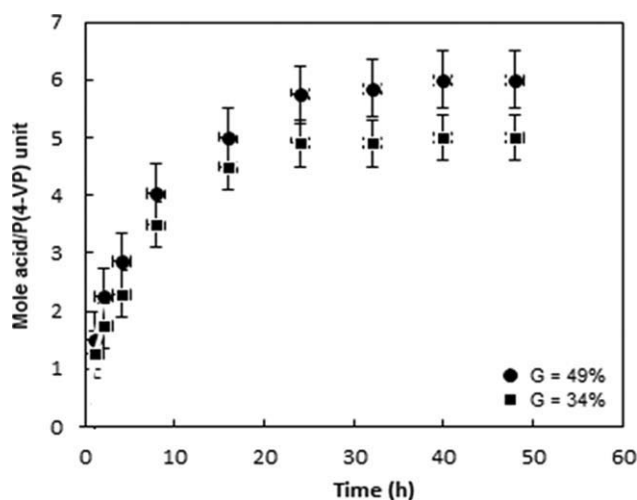
Figure 5. Variation of phosphoric acid doping with time for two membranes with G of: (■) 34% and (●) 49%. Acid concentration, 85 wt % and temperature, 50°C.

Evidence of 4-VP Grafting and Phosphorylation

The FTIR spectra of poly(4-VP) grafted ETFE film compared to the respective original ETFE film and pure poly(4-VP) films are shown in Figure 6. The spectrum of ETFE displayed a broad characteristic band in the range of 1000–1400 cm^{-1} representing CF$_2$ groups. The spectrum of poly(4-VP) homopolymer showed three bands at 1250, 1450 and 1600 cm^{-1}, which are characteristics for C—N, C=C and C=N of the pyridine ring, respectively. Similar characteristic bands can be clearly seen in the spectra of poly(4-VP) grafted films confirming the grafting of 4-VP onto ETFE films. When the grafted films were doped with PA, membranes spectral modifications in the regions 2000–3500 and 800–1300 cm^{-1} were observed. Such wide spectral domains are obscured by the absorption due to hydrogen bonding and vibrations of hydrogen phosphate groups, respectively.[24] These results are in a complete agreement with the spectral analysis reported
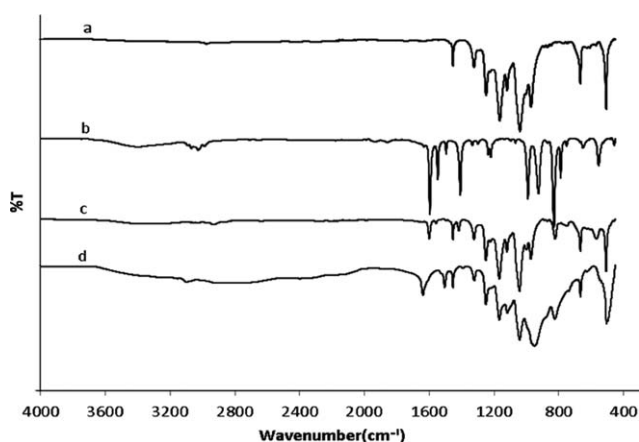

Figure 6. FTIR spectra of: a) original ETFE film, b) pure poly(4-VP) homopolymer, c) poly(4-VP) grafted ETFE films ($G = 47\%$), and d) phosphoric acid doped membranes ($G = 47\%$).
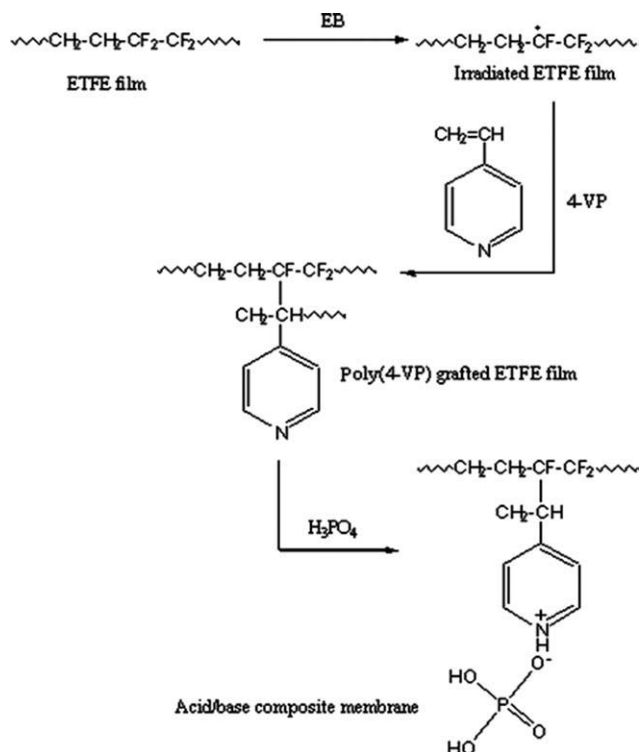

Figure 7. Plausible mechanism of preparation of phosphoric acid doped poly(4-VP) grafted ETFE membrane.

for phosphoric acid membranes in the literature.[8] Based on FTIR results it is reasonable to suggest the plausible mechanism shown in Figure 7 for PA doped membranes prepared in this study.

Structural Changes

X-ray diffractometry measurements were carried out to investigate the structural changes induced by the introduction of poly(4-VP) grafts to the ETFE films and subsequent PA doping as shown in Figure 8. Diffractograms of the original and poly(4-VP) grafted ETFE films [Figure 8(A)] shows an obvious decrease in the degree of crystallinity caused by grafting and the amount of such decrease is a function of $G\%$ i.e., higher $G\%$ leads to lower degrees of crystallinity and vice versa as illustrated from the inverse proportional relationship between the peak intensity and the degree of grafting. Doping with PA led to further decrease in the crystallinity of the grafted films and such decrease intensified with the increase in the content of poly(4-VP) grafts which hosts more acid as depicted in Figure 8(B). As grafting and subsequent acid doping produced no significant shifts in the angle ($2\theta = 19°$) compared with the original ETFE film, it can be fairly suggested that the reduction in the crystallinity of the membranes is due to the dilution effect on the inherent crystallinity of PVDF caused by the incorporation of amorphous poly(4VP)/PA complex without significant crystal disruption. Unlikely, grafting of polystyrene onto ETFE and its subsequent sulfonation led to a cumulative effect of dilution and partial disruption of the inherent crystallinity.[25] Such a discrepancy in the crystalline structure changes could be
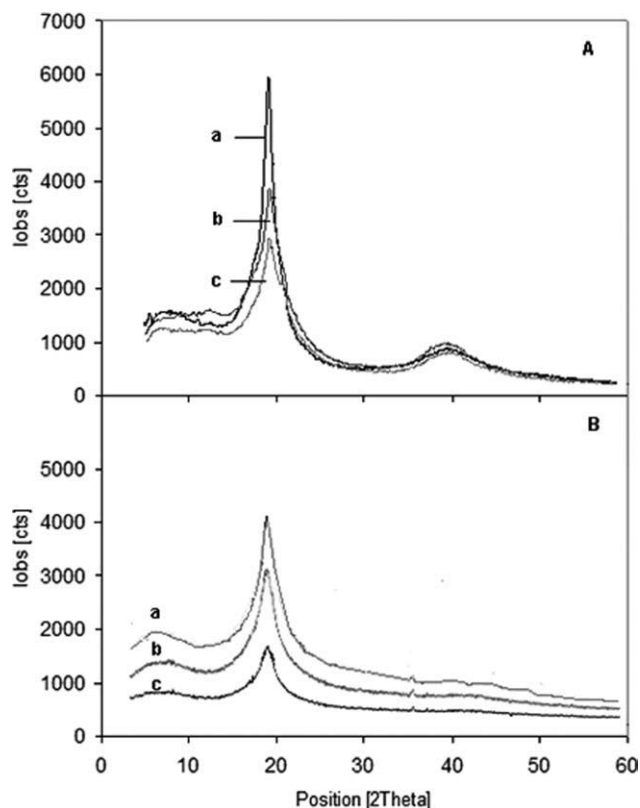
Figure 8. XRD diffractograms of (A) comparison between: a) original ETFE film and poly(4-VP) grafted ETFE films with G of; b) 28% and c) 49% and of phosphoric acid doped membranes having various degrees of grafting: a) 19%; b) 34% and c) 49%.

possibly due to the difference in the nature of the two reactions used to confer functional groups in the two types of membranes i.e., PA doping in this study and sulfonation of the benzene ring in Nasef et al.[25] The former involves acid/base complex interaction between PA and basic nitrogen of the pyridine ring of grafted poly(4-VP) through hydrogen bonding whereas the latter involves a substitution reaction on the benzene ring of the grafted polystyrene.

Thermal Stability
Figure 9 shows TGA thermograms of original ETFE film, poly(4-VP) grafted film and corresponding phosphoric acid doping membranes having two different degrees of grafting. The original ETFE film showed a single-step degradation pattern with transition at about 430°C due to the decomposition of molecular chains of ETFE film. The poly(4-VP) grafted film showed a two-step degradation pattern at 300 and 430°C due to the decomposition of poly(4-VP) grafts and the ETFE matrix, respectively. The phosphoric acid doped membrane showed a multistage degradation pattern as follows; (1) weight loss starts below 100°C and continues up to ~200°C, (2) at 200°C, (3) at 300°C, and (4) at 430°C. These results can be explained by taking the hygroscopic nature of the PA-doped membranes into account. The initial weight loss in stage 1 can be attributed to the loss of loosely bound water that was absorbed from atmospheric humidity upon storage by the membranes. The continuous

weight loss in step 2 is due to the decomposition of the protonated functional phosphoric acid groups. This can be explained by the continuous loss of water upon dehydration of PA molecules to diphosphoric acid:[26] $2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$. The weight loss in step 3 corresponds to the decomposition of the poly (4-VP) grafts of the membrane. The substantial weight loss in step 4 is due to the degradation of ETFE matrix. It can be noticed that the grafted film and PA membranes do not dissociate completely and some residues were left behind at the end of their thermograms unlike original ETFE film. This is most likely caused by the formation of inorganic residues containing N and C in the grafted film and P, N, and C in the PA membranes originated from poly(4-VP) and PA-doped poly(4-VP), respectively. These results are in a complete agreement with similar phosphoric acid doped membranes obtained by grafting of various basic vinyl monomer onto fluorinated polymer films.[8,27,28] Finally it can be suggested that the obtained membranes are suitable for PEM fuel cell operation below 200°C and have a thermal stability up to 160°C.

Mechanical Properties
The changes in tensile strength and elongation% at break for poly(4-VP) grafted film and their phosphoric acid counterparts were studied as a function of G% and the results are presented in Figure 10. It can be noticed that the tensile strength (TS) and the elongation percent (E%) decreased with the increase in G% in both grafted films and acid doped membranes with the latter attaining higher reduction in both mechanical properties. Such results were expected from the structural changes in the ETFE film upon the introduction of the amorphous poly(4-VP) grafts and subsequent phosphoric acid doping leading to the reduction in the crystallinity content with the increase in G%. However, the membranes maintained very reasonable mechanical properties at G equal to 34% (TS = 13.6 and E% = 161) and 49% (TS = 12.1 and E% = 137). Such combinations of mechanical properties seem to be suitable for making membrane/electrode assembly in high temperature PEM fuel cell application. A similar phosphoric acid doped membrane based on perfluorocyclobutyl/polybenzimidazole (PBI) showed lower
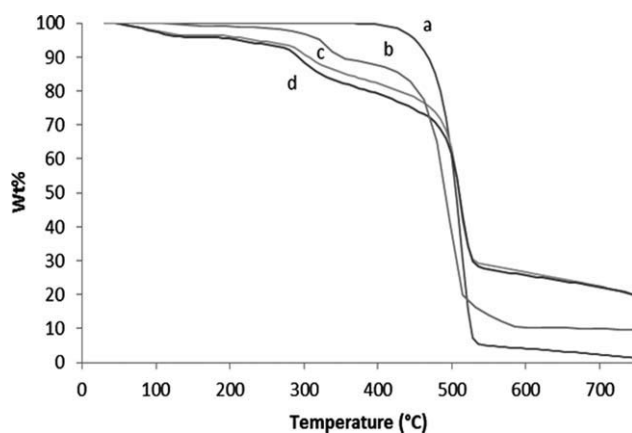

Figure 9. TGA thermograms of; a) original ETFE film, poly(4-VP) grafted ETFE films with G of 49%; phosphoric acid doped membrane with G of: c) 34% and d) 49%.
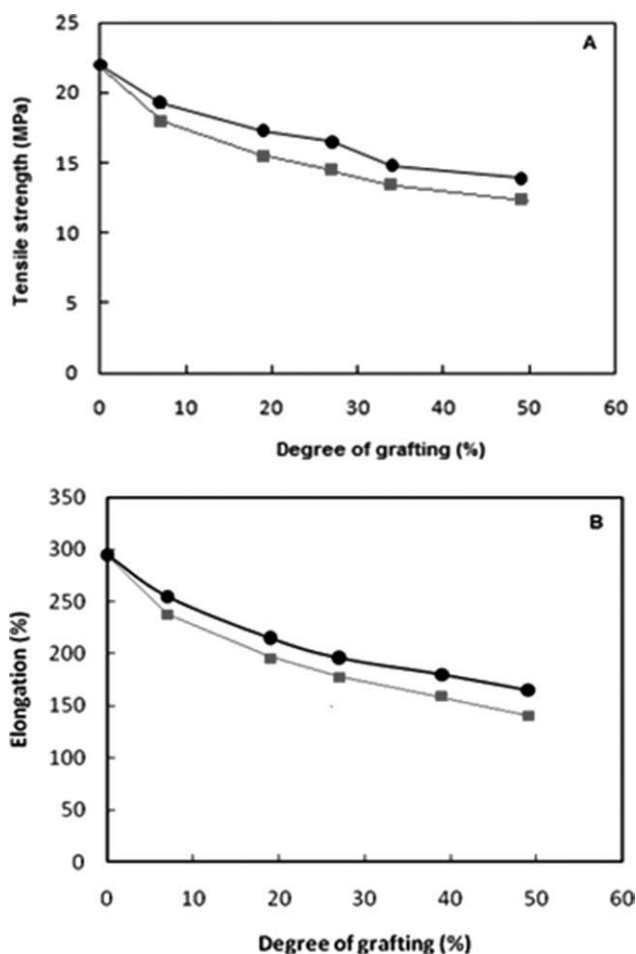
Figure 10. Variation of tensile strength (A) and elongation% (B) with degree of grafting before (●) and (■) after phosphoric acid doping.

mechanical properties (TS = 0.35 and $E\%$ = 130).[29] Another silica filled nanocomposite Nafion membrane was reported to have TS of 14.6 and $E\%$ of 78.9 compared with 15.9 and 156.4 for the corresponding cast Nafion, respectively.[30]
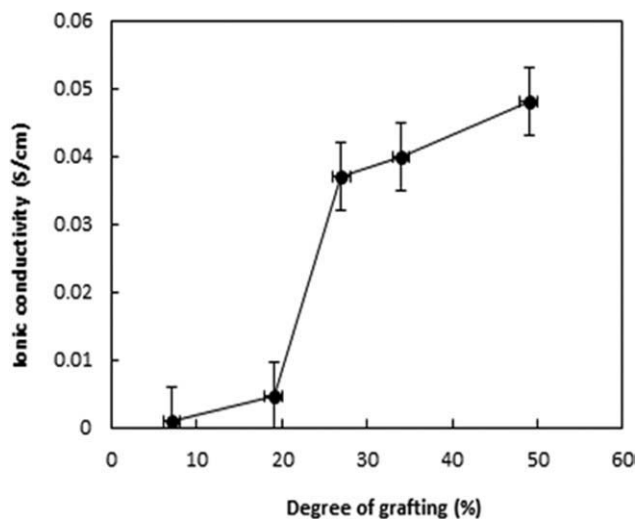

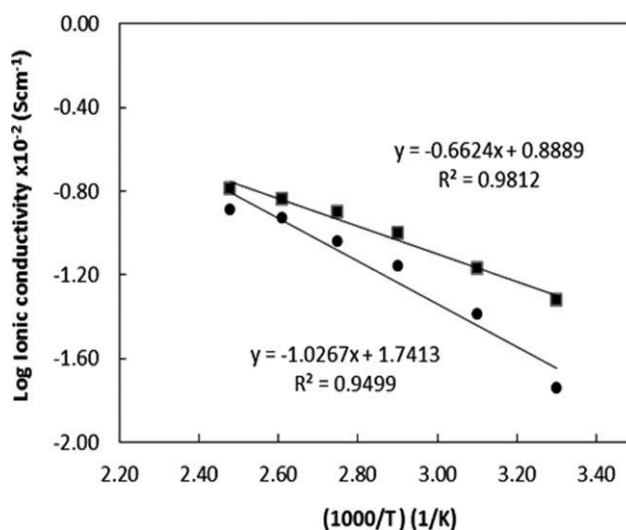**Figure 11.** Variation of the proton conductivity with degree of grafting.

Figure 12. Arrhinus plot for proton conductivity of phosphoric acid doped membrane at: 34% (●) and 49% (■) degrees of grafting.

Proton Conductivity

Figure 11 shows the relationship between the ionic conductivity and the degree of grafting. The proton conductivity increased with the increase in $G\%$ in the membranes at room temperature and achieved a value of 3.9 and 4.8 $\times$ 10^{-2} S/cm at $G\%$ of 34 and 49, respectively. This trend could be understood based on the fact that the increase in $G\%$ provides more $-N-$ sites for loading phosphoric acid in the membrane. Figure 12 shows the Arrhenius plot for proton conductivity of membranes having G of 34 and 49% and loaded with 5 and 6 mole of PA per repeating pyridine unit, respectively. As can be seen, proton conductivity increases with the increase in the temperature with the conductivity of 49% grafted membrane is higher than that of G = 34% at all temperatures. The observed linear dependence of proton conductivity of the membrane on the temperature following Arrhenius law suggesting the existence of a hopping-like conduction mechanism in the membranes. The activation energies between 30–130°C were calculated from the log ionic conductivity vs. 1000/T (K) and found to be 8.54 and 5.51 kJ mol^{-1} for 34 and 49% grafted membranes, respectively. Such low activation energy indicates that the incorporation of PA causes the formation of proton donor sites of NH^{+} in the membranes, which gets involved in H^{+} hopping from one the NH^{+} sites to phosphoric acid anions causing continuous proton transfer along the mixed anionic chains. The hopping increases with the increase in the temperature and this contribute significantly to the rise in the conductivity. A proton hopping along the H$_2$PO$_4^{-}$ anionic chain is also likely to contribute to the proton transfer and this is supported by the presence of high acid doping in these membranes. The presence of water in a form of bound water might also cause a proton hopping via water molecules contributing to proton conductivity but to a lower extent. These findings are going along with those reported for PA doped PBI.[31,24] However, the activation energy reported in this study is lower than that for PA-PBI members which was found to be in the range of 18–25 kJ mol^{-1} for an acid doping range from 2.0 to 5.6 mole.[28,32] Such discrepancy is possibly
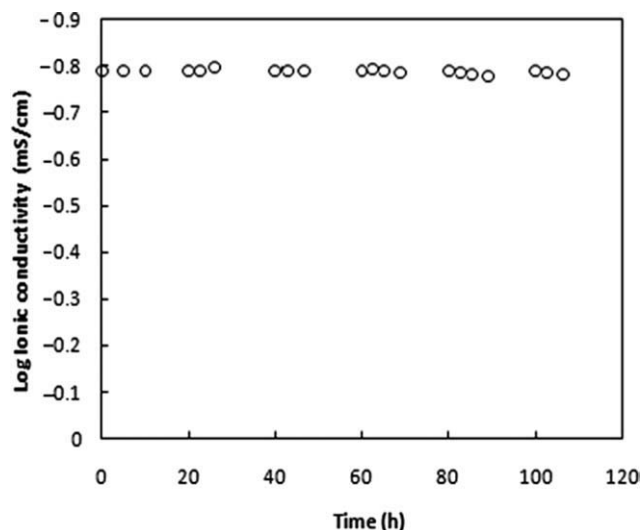
Figure 13. The ionic conductivity versus time for phosphoric acid doped membrane ($G = 49\%$) with 85% acid concentration. Sample was kept at 130°C.

due to the presence of additional NH available in the molecular structure of the PBI basic unit that may affect the proton hopping from one N—H site to another.

Stability of the Membranes

Figure 13 show the conductivity as a function of time of the membrane with $G = 49\%$. The membrane obviously shows stable proton conductivity without humidification for more than 100 h at a temperature of 130°C. This trend indicates the PA loaded sites in the membrane remain intact at the test temperature. Such finding also goes along with TGA analsys despite running the test under lower temperature. From this observation, one can suggest that the membrane has potential to be tested in PEM fuel cell operated above 100°C.

CONCLUSIONS

Preparation of acid/base composite membranes by radiation induced grafting of 4-VP onto ETFE films followed by phosphoric acid doping was successfully carried out under controlled conditions. The $G\%$ in the obtained membranes was found to be a function of the investigated grafting parameters. The mole of PA per repeating unit poly(4-VP) was found to be a function of reaction time and $G\%$. The incorporation of poly(4-VP) grafts and subsequent PA doping was proved by FTIR analysis. The proton conductivity of the membranes was found to be dependent on the degree of grafting and achieved a level of 10^{-2} S cm^{-1} magnitude in 34 and 49% grafted membranes at room temperature without humidification. The 49% grafted membrane showed a combination of unvaried proton conductivity (for 100 h) at 130°C with a thermal stability up to 160°C (as revealed by TGA analysis) together with reasonable mechanical properties. The results of this study suggest that grafting of 4-VP onto ETFE films followed by phosphoric acid doping provide an interesting route for preparation of less-water dependent composite acid/base membranes which have a strong potential for testing in PEM fuel cell operated above 100°C.

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