Synthesis and Characterization of Novel Graft Copolymers by Radiation-Induced Grafting

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ABSTRACT: The radiation-induced graft copolymerization of *N*-vinyl-2-pyrrolidone (NVP), 4-vinyl pyridine (4VP), and 2-vinyl pyridine (2VP) monomers onto poly (ethylene-*alt*-tetrafluoroethylene) (ETFE) was investigated. The influence of synthesis conditions particularly the solvent was studied. Various solvents, such as *n*-propanol, isopropanol, benzyl alcohol, methanol, ethanol, cyclohexanone, tetrahydrofuran (THF), nitromethane, 1,4-dioxane, and *n*-heptane were examined for this purpose. Graft copolymers were characterized by Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical analysis (DMA), and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDAX). It was found that the nature of the solvent had profound influence over the grafting reaction. Cyclohexanone, *n*-propanol, and isopropanol for 4VP/ETFE grafting, THF and 1,4-dioxane for NVP/ETFE grafting, and benzyl alcohol and methanol for 2VP/ETFE grafting were found to be the suitable solvents yielding highest graft levels. Isopropanol and *n*-propanol are promising in terms of both graft level and mechanical properties for 4VP/ETFE. Grafting of NVP, 4VP, and 2VP onto ETFE were verified through FTIR spectroscopy. Storage modulus and glass transition temperature of the copolymers were found to increase as graft level increased. Surface profile of representative films was also investigated by viewing the distribution of elemental nitrogen using SEM-EDAX. Results indicated that copolymers of 4VP, NVP, and 2VP are considerably different from each other. 4VP-based copolymers exhibited relatively more homogenous grafting over the surface compared with NVP- and 2VP-based copolymers. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2313–2323, 2011

Key words: graft copolymers; irradiation; membrane; solvent effect; fuel cell

INTRODUCTION

One of the commonly used methods for modifying the surface and bulk properties of polymeric materials is to graft monomers onto them by using an irradiation technique known as radiation-induced grafting. Radiation-induced grafting method has the advantages such as simplicity, low cost, control over process, and adjustment of the materials composition and structure. In addition, this method assures the grafting of monomers that are difficult to polymerize by conventional methods without residues of initiators and catalyst.[1] Radiation-induced grafting method is simply based on the irradiation of a base polymer either in the presence of a monomer (simultaneous radiation grafting) or without a monomer (preirradiation grafting) to create active sites as shown schematically in Figure 1.

Radiation grafting can also be used to combine the proton-conducting properties of a graft component with the thermal and chemical stability of the fluoropolymer base films together in membranes suitable for the application in Polymer Electrolyte Membrane Fuel Cells (PEMFC) and other electrochemical devices. It was previously reported that the favorable performance and durability of radiation-grafted membranes based on styrene and its derivatives for low-temperature PEMFC.[2–5] However, so far, only limited attention has been paid on the preparation of proton exchange membranes by radiation grafting for high-temperature fuel cell applications.[6]

In this study, nitrogen containing vinyl monomers, *N*-vinyl-2-pyrrolidone (NVP), 4-vinyl pyridine (4VP), and 2-vinyl pyridine (2VP) (Fig. 1) have been proposed as alternative grafting monomers to establish strong hydrogen bonding between N—H atoms that highly contributes to both ionic conductivity and durability of the membranes that will be used in high-temperature PEMFC. Poly (ethylene-*alt*-tetrafluoroethylene) (ETFE) has been employed as the base polymer for the preparation of membranes by radiation-induced grafting method due to its higher radiation stability and superior mechanical properties compared with perfluorinated polymers and better compatibility with the graft component.[3,7,8]

4VP has been studied previously due to its interesting property changes that can result from the
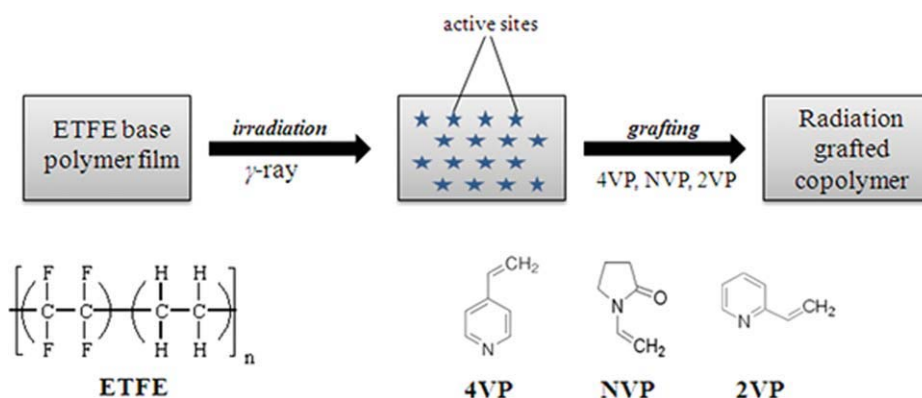
Figure 1 Radiation-induced grafting by preirradiation method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of the polar pyridine ring. Much previous work was oriented toward radiation grafting of 4VP into various base polymers including polyethylene,[9] polyvinylchloride,[10] styrene-butadiene-styrene triblock polymer,[11] poly(tetrafluoroethylene-*co*-hexafluoropropylene),[12] and there is only limited information on the optimization of grafting and characterization.[9–12] Grafting of NVP onto poly(tetrafluoroethylene),[13] low density polyethylene,[14] (tetrafluoroethylene-perfluorovinyl ether) copolymer,[15] poly(tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride),[16] and polypropylene[17] by radiation grafting was reported earlier only in a few studies. However, up to know, there are only two studies on radiation grafting of 2VP,[18,19] both are about the grafting of 2VP onto isotactic polypropylene. However, grafting of NVP, 4VP, and 2VP onto ETFE (as a base polymer) has never been investigated before. Moreover, no systematic research has been reported on the effect of grafting conditions. In addition, these monomers were not employed before for the preparation of proton exchange membranes for fuel cells by radiation grafting except for a study in literature in which 4VP was used.[6]

It is known that the use of solvents in radiation grafting enhances the accessibility of monomer to the grafting sites due to the ability of the solvent to swell the base polymer and the nature of the solvent may influence the grafting kinetics, the length of grafted chains, and the polymer microstructure. Correct choice of solvents is one of the essential elements toward the success of radiation-induced grafting process. There are only a few publications on the influence of solvents on radiation-induced grafting of different monomer/base film combinations.[12,20–23] However, research is still needed for understanding of the effect of solvents on grafting and properties of copolymers.

Consequently, not only the base polymer used but also grafting process (simultaneous radiation grafting, e-beam irradiation, high irradiation doses, grafting in aqueous media or bulk grafting, etc. were performed

mostly in literature) are very different from our current process and the resultant novel graft copolymers will exhibit quite different properties. Therefore, it is desirable to investigate both the grafting of these monomers onto ETFE and characterization of the resultant graft copolymers in detail.

This study concerns mainly the synthesis of graft copolymers using NVP, 4VP, and 2VP by radiation-induced grafting. Preirradiation grafting, which is only suitable for the grafting of crystalline base polymers where radicals remain trapped for a long period, was employed. Grafting conditions especially the effect of solvents during radiation grafting were investigated in detail. Moreover, resultant graft copolymers were characterized *ex situ* by Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical analysis (DMA), and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDAX).

The preparation of phosphoric acid-based membranes for high-temperature fuel cells from the copolymers synthesized in this study are under investigation and will be the topic of further publications.

EXPERIMENTAL

Materials

The base polymer poly(ethylene-*alt*-tetrafluoroethylene), or ETFE, was purchased in the form of a 25-μm thick film (Nowoflon ET-6235) from Nowofol GmbH (Siegsdorf, Germany). The reagents used during membrane preparation, monomers (NVP, 4VP, and 2VP), and solvents (Sigma Aldrich), were used without any further purification.

Radiation-induced grafting

The base polymer, ETFE was cut into 7 cm × 7 cm, washed with ethanol, and then, 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 10–50 kGy. After exposure, the films were stored at −80°C until used.

Irradiated films were placed into glass tube reactors and then grafting solution composed of monomer and solvent was added to reactors which were then purged with dry nitrogen for 30 min. The reactors were subsequently sealed and placed in thermostated water bath, and grafting reactions were carried out certain times to achieve reasonable grafting by irradiation dose. The grafted films were washed with the solvent used during grafting to remove residual monomer and/or polymer, which were not bonded to the base film, then dried at 70°C and reweighed.

The extent of graft polymerization, grafting percentage, or graft level (GL) is calculated as follows:

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

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

Fourier transform infrared spectroscopy

The structure of both the base polymer film and the graft copolymer films was analyzed by FTIR spectroscopy. Measurements were carried out with a Bruker Equinox 55 FTIR spectrometer in absorbance mode in a wave number range of 4000 cm^{-1} to 500 cm^{-1}.

Dynamic mechanical analysis

Mechanical properties of the resultant graft copolymers were studied by a Netzsch 242C dynamic mechanical analyzer (DMA). The measurements were done in the tensile mode at an oscillation frequency of 1 Hz. The dimensions of the test films were ∼ 0.5 mm in width and 2 mm in length. The sinusoidal amplitude of strain was applied during the temperature sweep from 25 to 200°C at a rate of 1°C/min. The value of glass transition temperatures was evaluated from the loss tangent (tan δ) curve as the maximum of the peak.

$$\tan\ \delta = \frac{E''}{E'}$$

where E'' is loss modulus and E' is storage modulus of the graft copolymer.

Scanning electron microscopy-energy dispersive spectroscopy

SEM-EDAX (Supra 35VP, Leo, Germany) measurement was conducted to investigate the nitrogen dis-
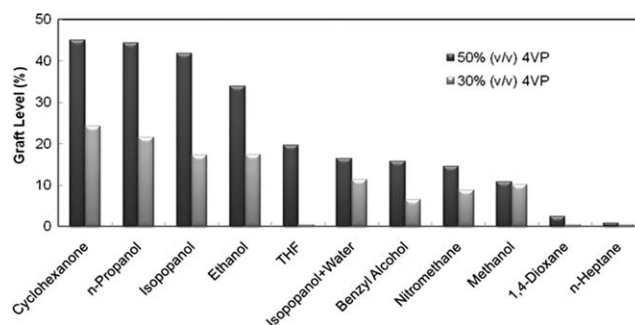
Figure 2 Effect of solvent on graft level (%) for 4VP grafting onto ETFE at different 4VP concentrations. Grafting conditions: 25 μm ETFE, 10 kGy, 60°C.

tribution on the surface of the copolymer films. An accelerating voltage of 10 kV was used during the measurements.

RESULTS AND DISCUSSION

Radiation-induced grafting

Radiation-grafted copolymers based on three different nitrogen containing vinyl monomers were synthesized in various solvents including; n-propanol, isoproponol, benzyl alcohol, methanol, ethanol, cyclohexanone, THF, nitromethane, 1,4-dioxane, and n-heptane. The resultant copolymers from 4VP/ETFE, NVP/ETFE, and 2VP/ETFE grafting were abbreviated as ETFE-g-P4VP, ETFE-g-PNVP, and ETFE-g-P2VP, respectively.

Figure 2 represents the variation of graft level for 4VP grafting onto ETFE in different solvents. Two different 4VP concentrations, 30% (v/v) and 50% (v/v), were employed. Because of the high reactivity of 4VP, desired graft levels can be achieved by using short reaction time and low irradiation dose which has the advantage of reduced radiation damage to the base polymer. It is evident that higher monomer concentration yielded higher graft levels due to the availability of monomer at grafting sites.

It was found that graft level of the copolymers was strongly dependent on the type of solvent used during grafting. Graft levels of ETFE-g-P4VP copolymers decrease in the order of cyclohexanone > n-propanol > isoproponol > ethanol > THF > benzyl alcohol > nitromethane > methanol > 1,4-dioxane > n-heptane.

The radiation grafting reaction is governed by the diffusion of monomers into the base film, step growth reaction of the grafted chains, and termination reactions. Since the base polymer films are insoluble in all common solvents and barely swell, grafting takes place at the film surface and behaves as the grafting front. This grafted layer swells in the reaction medium and further grafting proceeds by the progressive diffusion of the monomer through

Solvent	Solubility parameter δ (cal/cm^3)$^{1/2}$
n-Heptane	7.4
Tetrahydrofuran	9.1
Cyclohexanone	9.9
1,4-Dioxane	10.0
4-Vinil pyridine	11.0
Isopropanol	11.5
n-Propanol	11.9
Benzyl alcohol	12.1
Nitromethane	12.7
Ethanol	12.7
Methanol	14.5
Isopropanol–Water	19.0

this swollen layer and grafting front movement to the middle of the film. This mechanism is known as grafting front mechanism.[24] Grafting occurs uniformly and smoothly in a solvent which provides the swelling of grafting front. The diffusion of the monomer to the base polymer and swelling of grafting front are mainly determined by the solubility parameters of the grafting components (solvent, monomer/polymer). As shown in Figure 2, high graft levels achieved in cyclohexanone, *n*-propanol, and isopropanol can be explained by the close proximity of solubility parameters of these solvents with 4VP and poly(4-vinyl pyridine).[25] Similarly, *n*-heptane yielded the lowest graft level due to the large difference in solubility parameters. Higher graft levels obtained in ethanol compared with those in methanol could be also attributed to the much closer solubility parameter ethanol than that of methanol. Solubility parameters of solvents employed in this study are given in Table I.[25]

Although, benzyl alcohol, nitromethane, and 1,4-dioxane have similar solubility parameters with 4VP and poly(4-vinyl pyridine), graft levels obtained in these solvents were too low. This behavior can be accounted for chain transfer to solvent. It is known that low graft levels are obtained with solvents having high chain transfer constants; hence, the growing chains will be readily terminated. Benzyl alcohol, nitromethane, and 1,4-dioxane have high chain transfer constants leading to lower graft levels. Moreover, significant amount of homopolymer formation due to the chain transfer reactions was observed for grafting of 4VP monomer in benzyl alcohol, 1,4-dioxane, and nitromethane. Therefore, the graft copolymers obtained in these solvents were subsequently washed with solvents and soaked overnight to remove homopolymer. On the other hand, as reported earlier[27] for both 4VP and 2VP polymerizations, the chain transfer constants to aliphatic alcohols were found to be too low which can be another reason of high graft levels in *n*-propanol,

isopropanol, and ethanol. According to previous findings of styrene/ETFE grafting, significantly enhanced graft levels were obtained with the addition of water to isopropanol.[28] Polar solvents such as alcohols in combination with water were found to yield high grafting rates. This means that the grafting times are short or the irradiation dose of the base polymer can be reduced which leads the less radiation damage of the material. However, no improvement was detected for 4VP/ETFE grafting in isopropanol–water system, since addition of water increases the difference in solubility parameters.

Same tendency of graft levels with respect to solvents was observed for both 4VP concentrations [30% (v/v) and 50% (v/v)] except for THF. Surprisingly, it was found that THF yielded reasonable graft levels for 50% (v/v) 4VP, whereas very low graft levels were obtained for 30% (v/v) 4VP. It was observed experimentally that at low 4VP concentrations [30% (v/v)] homopolymer formation was significant when monomer was introduced to THF. Consequently, most of the monomer was converted to homopolymer before grafting to base film; so, graft levels were too low in that case. At high 4VP concentration, homopolymer formation was still predominant but there may be some monomer remained for the grafting to the base film.

It was reported previously the influence of various solvents on radiation-induced grafting of 4VP onto polyethylene,[9] poly(vinyl chloride),[10] styrene-butadiene-styrene triblock copolymer, and [11] poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP).[12] Compared with our work, the diversity of the results may be due to the differences of grafting method (simultaneous grafting used in literature) and base film type.

To the best of our knowledge, there were no previous studies on the synthesis of NVP-based copolymers by radiation-induced grafting of NVP onto ETFE. Therefore, NVP/ETFE grafting was more focused in this study. Grafting in various solvents, several irradiation doses, and different NVP concentrations have been studied. As far as the different NVP concentrations are concerned, graft level increases as the monomer concentration increases, reaching a maximum value at 50% (v/v) NVP, and then decreases abruptly at higher monomer concentration [80% (v/v) NVP] [Fig. 3(a)]. This may be due to the limited diffusion of the monomer into the film, which is low in the case of high monomer concentration. At high monomer concentrations, the complexity arising from the extensive homopolymerization during the grafting may hinder monomer diffusion to the radical sites and may lead to diminishing grafting. This may lead to the maxima at specific monomer concentrations, beyond which the grafting would decrease rapidly.[1,28] In such a case,
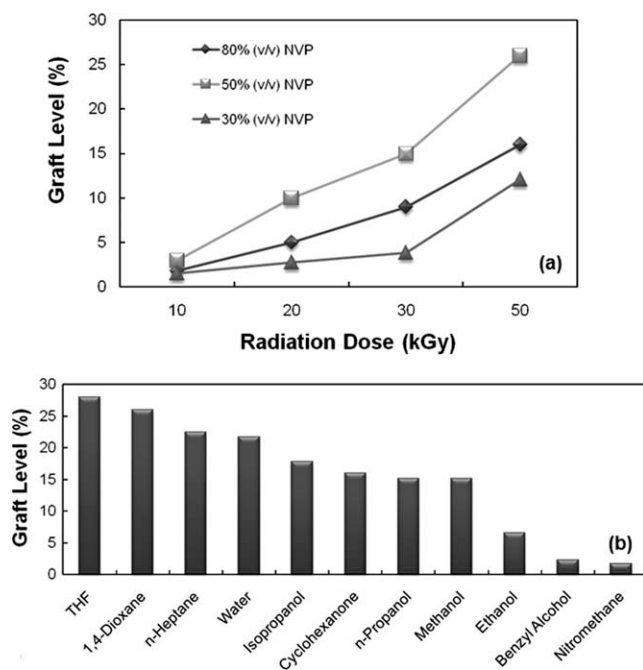
Figure 3 (a) Variation of graft level (%) as a function of irradiation dose for NVP grafting onto ETFE at different NVP concentrations. Grafting conditions: 25 μm ETFE, 50 kGy, 60°C, in 1,4-dioxane. (b) Effect of solvent on graft level (%) for NVP grafting onto ETFE. Grafting conditions: 25 μm ETFE, 50 kGy, 60°C, 50% (v/v) NVP.

the trapped radicals can recombine readily and homopolymerization which increases the viscosity of the solution occurs intensively. Eventually, the graft level decreases.

Figure 3(a) exhibits also that as the irradiation dose increases, graft levels of ETFE-g-PNVP copolymer increase dramatically owing to the increased concentration of free radicals on the base film.[28] Since desired graft levels were achieved with 50% (v/v) NVP concentration and ETFE films irradiated with 50 kGy, these conditions were selected as the optimum conditions at which the rest of experiments were performed.

Figure 3(b) indicates the variation of graft level of ETFE-g-PNVP copolymer with respect to solvents studied. It was found that graft levels decrease in the following sequence: THF > 1,4-dioxane > n-heptane > water > isopropanol > cyclohexanone > n-propanol > methanol > ethanol > benzyl alcohol > nitromethane.

THF and 1,4-dioxane, having solubility parameters close to that of poly(N-vinyl 2-pyrrolidone) or PNVP (10.1–13.7),[26] are likely to be the suitable solvents for NVP grafting to ETFE. Isopropanol, cyclohexanone also yielded reasonable graft levels by the similar reason. However, high graft levels obtained in n-heptane and water or very low graft level obtained in nitromethane and benzyl alcohol cannot be explained by solubility parameters. High chain

transfer constants of nitromethane and benzyl alcohol may be the reason of low graft levels as found in 4VP/ETFE. Moreover, water serves as a suitable solvent for NVP grafting may be due to its low chain transfer constant, which enhances graft level or its polarity, which aids the swelling of the grafted layer when the hydrophilic monomers were grafted onto ETFE.

Hegazy et al. reported on simultaneous radiation grafting of aqueous NVP onto low density polyethylene[14] and poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether)[15] previously. They pointed out the significant amount of homopolymer formation during grafting if no inhibitor was used. Graft levels about 20% was obtained with irradiation dose of 58 kGy and 50% (v/v) NVP that in the presence of $CuCl_2$ as inhibitor to prevent homopolymerization in simultaneous grafting in their work. Even though preirradiation gives lower graft levels than that of simultaneous irradiation, we obtained much better graft levels without using an inhibitor as no homopolymerization was observed in our case. In another previous study, simultaneous-radiation grafting of NVP onto poly(tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride) using different solvents was described.[16] Although a different base polymer was used, and authors found high graft levels in 1,4-dioxane which is in agreement with our study. On the contrary, very high graft levels (up to 200%) were reported previously for simultaneous grafting of NVP onto polypropylene in dimethyl formamide using an inhibitor.[17]

Similar to NVP case, nobody reported on radiation-induced grafting of 2VP onto ETFE up to know. From the screening experiments for 2VP grafting onto ETFE, it was observed that 2VP is less reactive compared with 4VP and NVP. Thus, as a first attempt, relatively high irradiation dose was examined. Figure 4(a) presents the variation of graft levels with respect to solvents at two different irradiation doses, 10 kGy and 50 kGy, that for 2VP grafting onto ETFE. Although higher graft levels were obtained at 50 kGy, the improvement was not substantial compared with 10 kGy. This may be due to the decomposition of radicals and of recombination or transfer reactions that is expected to occur to some extent by an increasing dose. As a second attempt, the reaction temperature increased to achieve reasonable graft levels since temperature increase is expected to enhance not only the diffusion of monomer toward active sides of base film and the advancement of the grafting front but also the reactivity of radicals.[1,28] Figure 4(b) shows the variation of graft level with solvents at two different grafting temperatures (60°C and 90°C). It was found that graft levels obtained at different temperatures were not significantly different. In grafting process,
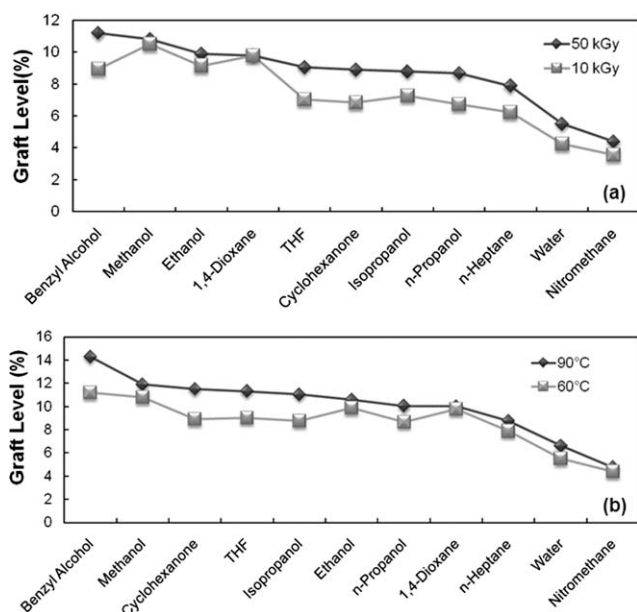
Figure 4 (a) Effect of solvent on graft level (%) for 2VP grafting onto ETFE at irradiation doses of 10 kGy and 50 kGy. Grafting conditions: 25 μm ETFE, 60°C, 50% (v/v) 2VP. (b) Effect of solvent on graft level (%) for 2VP grafting onto ETFE at temperatures of 60°C and 90°C. Grafting conditions: 25 μm ETFE, 50 kGy, 50% (v/v) 2VP.

grafted zone remains swollen which leads to high mobility of the growing chains within polymer matrix. Therefore, termination of the two growing chains by mutual combination becomes dominant at higher temperatures. At the same time, the primary radical termination may also be accelerated by the time the monomer reaches their vicinity. In addition to that, the increase of the reaction temperature enhances the production of homopolymer in the grafting solution and then the diffusion of the monomer is hindered.[28] All these can be regarded as the reasons of low graft levels.

The order of graft levels with respect to solvent for 2VP/ETFE grafting at 50 kGy and 60°C were determined as follows: benzyl alcohol > methanol > ethanol > 1,4-dioxane > THF > cyclohexanone > isopropanol > n-propanol > n-heptane > water > nitromethane. High graft levels obtained in ethanol, 1,4-dioxane, THF, cyclohexanone, isopropanol, and n-propanol can be ascribed to the closeness of the solubility parameters of these solvents to that of poly(2-vinyl pyridine) [10.4 (cal/cm^3)$^{1/2}$].[29] The dominance of alcohols in high graft levels for 2VP grafting are probably due to low chain transfer constants of alcohols based on a similar reasoning as earlier. As the nitrogen atom that is situated at the α-position of pyridine has a lone electron pair and shows basic character due that the solubility is greater in an alcohol. However, except for alcohols, the order of graft levels with respect to solvent type

was found to be significantly different for these isomeric monomers, 2VP and 4VP.

As mentioned at very beginning of this article, there were only two studies on radiation induced grafting of 2VP in literature.[18,19] Authors performed 2VP grafting in the presence of styrene as a second monomer onto isotactic propylene. High graft levels in water and methanol–water were reported. It should be noted though that those earlier results and the present ones are not necessarily directly comparable since the base polymers are different. Therefore, different radical concentrations produced by the irradiation, different structures of the radical centers, variations in crystallinity and glass transition may result in differences in grafting of 2VP.
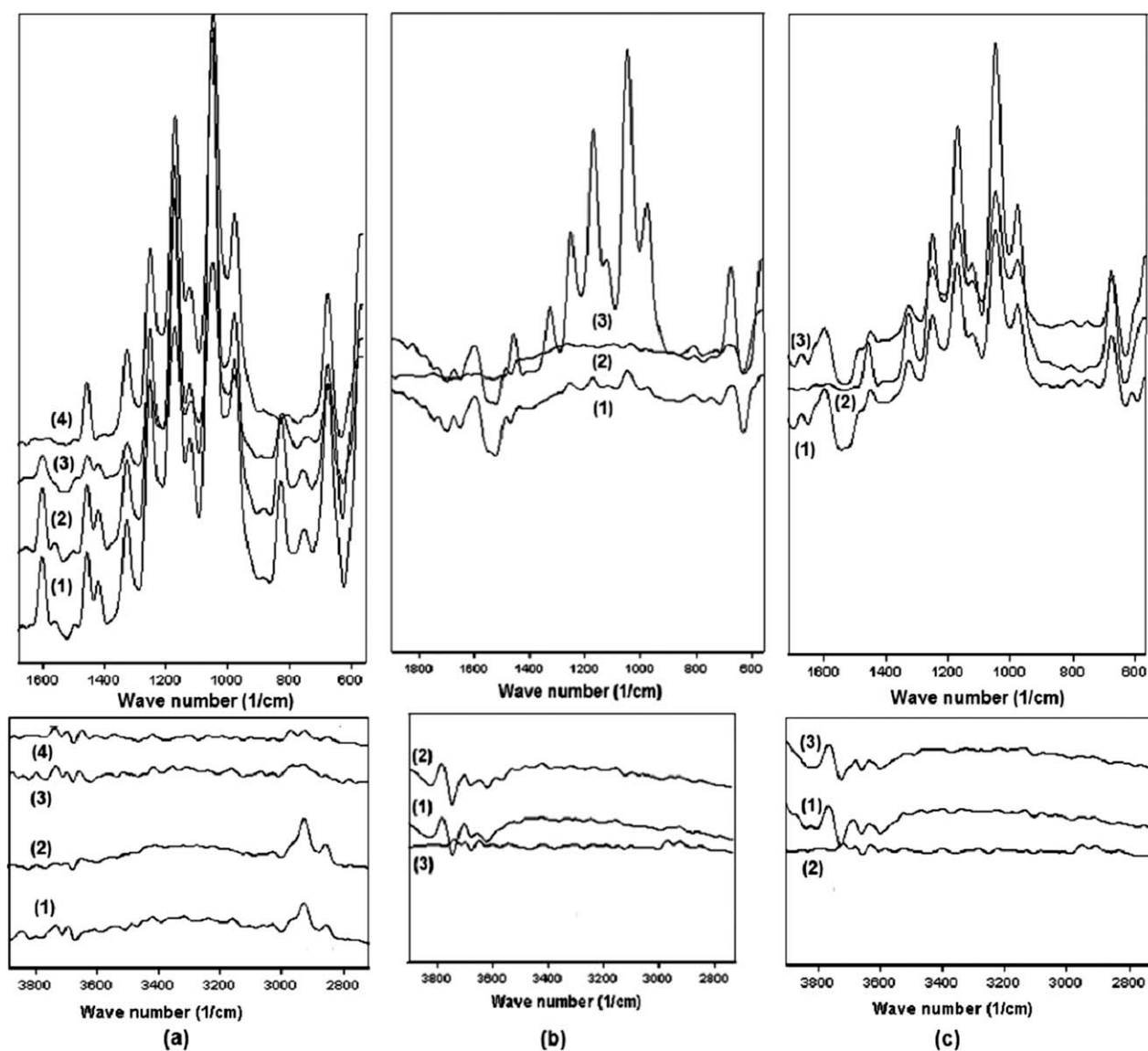
Fourier transform infrared spectroscopy

FTIR spectroscopy was performed for both ETFE base film and graft copolymers to investigate whether the monomer is incorporated with base film or not. Graft copolymers with high graft levels obtained in promising solvents were analyzed for this purpose.

Figure 5(a) shows the FTIR spectra of the ETFE-g-P4VP copolymers synthesized in different solvents and ETFE base polymer film. ETFE base film is initially characterized by the presence of strong bands in the range of 1000 to 1400 cm^{-1} which are characteristics for CF$_2$ groups. Moreover, symmetric and asymmetric stretching vibrations of CH$_2$ groups at 2921 cm^{-1} are present in ETFE base film. The peak at 1598 cm^{-1} attributed to C=N bond, and the peak at 1452 cm^{-1} attributed to C=C bonds of 4VP are present in ETFE-g-P4VP.[30] A band at 1248 cm^{-1} due to the C—N vibration of 4VP also exists in ETFE-g-P4VP. The less intense peak at 3730 cm^{-1} belongs to the N—H bonds. Therefore, observed differences between the FTIR spectra of ETFE and those of graft copolymers verified the existence of grafting.

The FTIR spectra of the ETFE-g-PNVP copolymers synthesized using promising solvents and ETFE base film are given in Figure 5(b). Compared with FTIR spectrum of ETFE base polymer, the appearance of new peaks at 1596 cm^{-1}, 1248 cm^{-1}, 1452 cm^{-1} are characteristics to C=O bond, C—N bond, and C=C bond, respectively. In the case of NVP grafting 1590 cm^{-1} that signify the characteristic C=O bond of NVP is distinguished. The peak at 3780 cm^{-1} belongs to the N—H bonds are also observed. As conclusion, grafting of NVP into ETFE film was verified.

FTIR spectra of ETFE-g-P2VP copolymers synthesized in benzyl alcohol and methanol and ETFE base polymer film are depicted in Figure 5(c). The peaks correspond to C=C and C=N of pyridine at 1452 cm^{-1} and 1593 cm^{-1}, respectively, and a band

Figure 5 (a) Fourier transform infrared (FTIR) spectra of (1) ETFE-*g*-P4VP in synthesized isopropanol, (2) ETFE-*g*-P4VP synthesized in *n*-propanol, (3) ETFE-*g*-P4VP synthesized in cyclohexanone, and (4) ETFE base film. (b) FTIR spectra of (1) ETFE-*g*-PNVP synthesized in 1,4-dioxane, (2) ETFE-*g*-PNVP synthesized in THF, and (3) ETFE base film. (c) FTIR spectra of (1) ETFE-*g*-P2VP synthesized in methanol, (2) ETFE base film, and (3) ETFE-*g*-P2VP synthesized in benzyl alcohol.

at 1247 cm^{-1} due to the C—N vibration of 2VP are present in ETFE-*g*-P2VP proved the grafting of 2VP.[31] Again, the peak at 3700 cm^{-1} belongs to the N—H bonds.

Dynamic mechanical analysis

Mechanical behavior of the graft copolymers used for the preparation of fuel cell membranes are important in terms of handling, fabrication of membrane electrode assemblies and to offer a durable material. Moreover, the structural changes and the degradation are usually reflected in the mechanical properties of the copolymers. Thus, it is of interest to investigate the dynamic mechanical properties of graft copolymers synthesized in this study.

The temperature dependence of loss tangent (tan δ) and storage modulus of graft copolymers are depicted in Figures 6–8. Single broad peaks can be observed in tan δ versus temperature plots [Figs. 6(a), 7(a), and 8(a)] for each of the copolymers investigated. Single peaks may indicate that there is no phase separation. The maximum of tan δ peaks corresponds to glass transition temperature (T_g) for each case. First of all, as graft level increases, the tan δ maximum shifts to higher temperature which indicates the increase of T_g. For instance, the T_g values for ETFE-*g*-P4VP copolymers synthesized in isopropanol with graft level of 41%, in *n*-propanol with graft level of 45%, and in cyclohexanone with graft level of 48% were determined as 130°C, 140°C, and 150°C, respectively, [Fig. 6(a)]. Similarly, T_g values
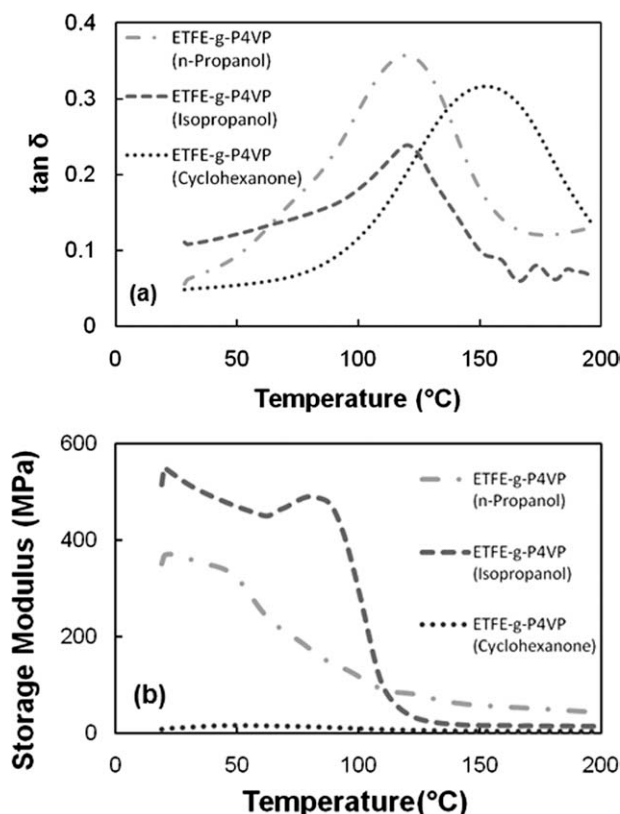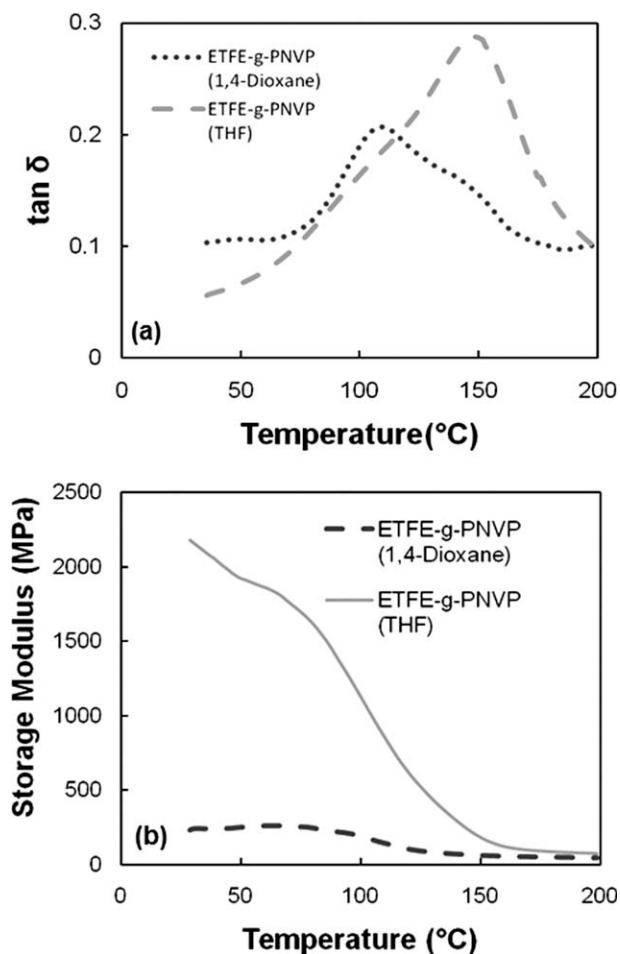
Figure 6 (a) The temperature dependence of loss tangent (tan δ) of ETFE-*g*-P4VP (GL: 45%, synthesized in *n*-propanol), ETFE-*g*-P4VP (GL: 41%, synthesized in isopropanol), ETFE-*g*-P4VP (GL: 48%, synthesized in cyclohexanone) and (b) The temperature dependence of storage modulus of ETFE-*g*-P4VP (GL: 45%, synthesized in *n*-propanol), ETFE-*g*-P4VP (GL: 41%, synthesized in isopropanol), ETFE-*g*-P4VP (GL: 48%, synthesized in cyclohexanone).

for ETFE-*g*-PNVP copolymer with graft level of 26% in 1,4-dioxane was 110°C and the copolymer with graft level of 28% in THF was 150°C [Fig. 7(a)]. Correlatively, ETFE-*g*-P2VP copolymers with a graft level of 12% in methanol and 14% in benzyl alcohol exhibit T_g values at 90°C and 110°C, respectively, as shown in Figure 8(a). T_g of ETFE base film was reported as 110 to 135°C in literature.[32–34] The difference in literature values of ETFE base polymer may be resulted from the type of ETFE film (different molecular weight, etc.) and different measurement technique. The increase of T_g with graft level can be attributed to the restrictions in the movements of polymer due to the incorporation of glassy graft chains to the ETFE base film. As expected, the monomer and the solvent employed during grafting influence the T_g of resultant copolymers to different extent.

Figure 7(b) shows the variation of storage modulus with respect to temperature for the ETFE-*g*-P4VP copolymers with different graft levels and synthesized in isopropanol, *n*-propanol, and cyclohexanone. In the temperature region investigated, the

minimum storage modulus values was obtained for the copolymer obtained in cyclohexanone which was experienced as wrinkled, rough, uneven, and brittle films as well. Copolymer obtained in isopropanol possessed relatively higher storage modulus values compared with the one from *n*-propanol up to 110°C after which comparable values were obtained.

The graft level is one of the important quantities which has a direct and major influence on different *ex situ* and *in situ* properties of the grafted films and, subsequently on the membranes. High graft levels of copolymers and resultant membranes are preferred to obtain high ionic conductivity. However, high graft levels may result in the deterioration of some mechanical properties. Therefore, it is necessary to find a compromise between the mechanical robustness of the membrane and its proton conductivity. As a consequence, although cyclohexanone yielded the highest graft level, *n*-propanol and isopropanol were found to be the most promising

Figure 7 (a) The temperature dependence of loss tangent (tan δ) of ETFE-*g*-PNVP (GL: 28%, synthesized in THF), ETFE-*g*-PNVP (GL: 26%, synthesized in 1,4-dioxane) and (b) The temperature dependence of storage modulus of ETFE-*g*-PNVP (GL: 28%, synthesized in THF), ETFE-*g*-PNVP (GL: 26%, synthesized in 1,4-dioxane).
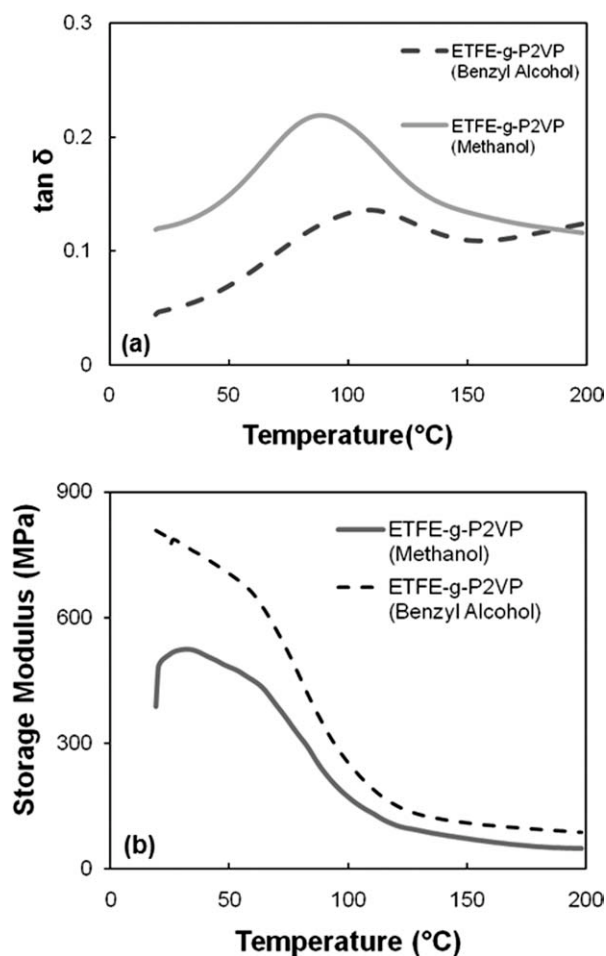
Figure 8 (a) The temperature dependence of loss tangent (tan δ) of ETFE-*g*-P2VP (GL; 14%, synthesized in benzyl alcohol), ETFE-*g*-P2VP (GL: 12%, synthesized in methanol) and (b) The temperature dependence of storage modulus of ETFE-*g*-P2VP (GL; 14%, synthesized in benzyl alcohol), ETFE-*g*-P2VP (GL: 12%, synthesized in methanol).

solvents to obtain both high graft levels and reasonable mechanical properties to synthesize ETFE-*g*-P4VP.

As far as the storage modulus values of ETFE-*g*-PNVP and ETFE-*g*-P2VP are concerned, both decline sharply as the temperature increases [Figs. 7(b) and 8(b)]. It can be seen from Figure 7(b) that the storage modulus values of ETFE-*g*-PNVP (in THF) at lower temperature is larger than that of ETFE-*g*-PNVP (in 1,4-dioxane), which indicates ETFE-*g*-PNVP synthesized in THF has higher stiffness. It is found that THF is the most promising solvent for NVP monomer in terms of graft level and the strength of graft copolymer. Storage modulus values of ETFE-*g*-P2VP copolymer from benzyl alcohol were higher than those from methanol but their difference was not so noticeable at temperatures above 100°C. Therefore, both benzyl alcohol and methanol can be regarded as the most favorable solvents for 2VP grafting onto ETFE in the sense of graft level and mechanical properties.

As seen in the case of ETFE-*g*-PNVP and ETFE-*g*-P2VP copolymers at low temperatures, the increase of graft level caused to an increase in storage modulus which is an indication of the increased stiffness of copolymers. That may probably be due to the steric hindrance of the bulky pyridine and pyrrolidone groups which results in a stiffer polymer chain.

Scanning electron microscopy-energy dispersive spectroscopy

The uniform distribution of the grafts is an important factor along with graft level in both copolymers and the resultant membranes to have homogenous ion exchange mechanism. The graft copolymer films synthesized in this study were found to be homogeneous in appearance especially for higher graft levels. However, we know that it is not always possible based on our previous experience. Therefore, we analyzed the surfaces of the graft copolymer films by SEM-EDAX. Since nitrogen is known to be mainly introduced to copolymer structure by grafting of nitrogen containing 4VP, NVP, and 2VP, it can be assumed that the
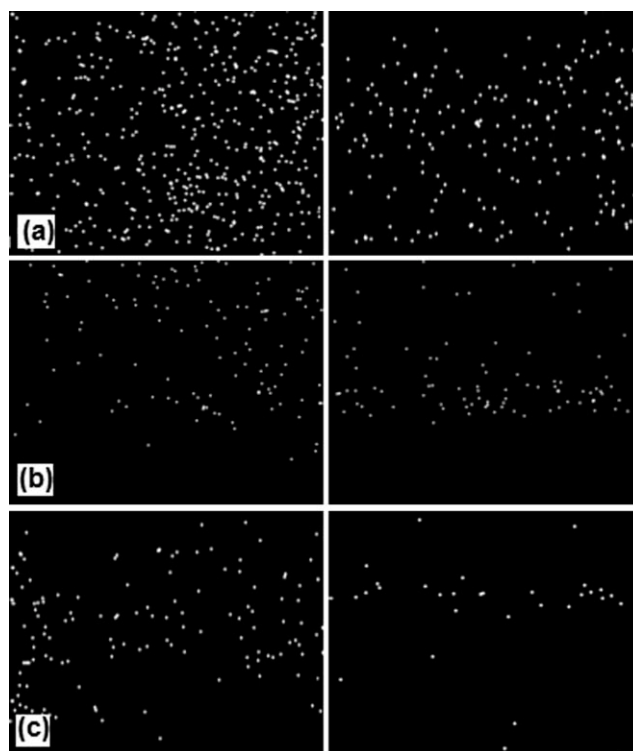
Figure 9 (a) Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDAX) micrographs of N mapping for ETFE-*g*-P4VP, GL: 48% synthesized in cyclohexanone (left) and GL: 16% synthesized in benzyl alcohol (right), (b) SEM-EDAX micrographs of N mapping for ETFE-*g*-PNVP, GL: 28% synthesized in THF (left) and GL: 2% synthesized in nitromethane (right), and (c) SEM-EDAX micrographs of N mapping for ETFE-*g*-P2VP, GL: 14% synthesized in benzyl alcohol (left) and GL: 5% synthesized in nitromethane (right).

distribution profile of the nitrogen corresponds to that of the P4VP, PNVP, and P2VP grafts.

Figure 9 demonstrates the SEM-EDAX images in which white dots are representative of nitrogen of the graft copolymers. It was found that these copolymers were substantially different from each other. In the case of ETFE-*g*-P4VP copolymer, nitrogen was almost uniformly distributed on the surface for the film with having graft level of 48% (in cyclohexanone), whereas less homogenous nitrogen distribution was observed for the film with 5% graft level (in benzyl alcohol) [Fig. 9(a)].

The copolymers of ETFE-*g*-PNVP and ETFE-*g*-P2VP showed relatively uneven and lower nitrogen content at the surface of films compared with ETFE-*g*-P4VP copolymer. This behavior was much more pronounced in the case of copolymers with low graft levels [Fig. 9(b,c)].

As conclusion, the distribution of nitrogen was strongly influenced by not only the graft levels of the copolymers but also the nature of the grafting medium which takes into account both the monomers and the solvents. The graft level is a bulk property and is averaged over the film thickness and area. At low grafting, the graft distribution was heterogeneous on the surface; however, at high grafting, the surface became more homogenous.

CONCLUSIONS

Graft copolymers using NVP, 4VP, and 2VP were synthesized by radiation-induced grafting. Grafting of 4VP onto preirradiated ETFE films has been shown to be possible with high graft levels by employing short reaction time and low irradiation dose (10 kGy) which has the advantage of reduced radiation damage on the base polymer structure due to the high reactivity of 4VP. In the case of both NVP and 2VP grafting onto preirradiated ETFE films, relatively higher irradiation doses (30 and 50 kGy) were required.

The application area of the resultant graft copolymers is targeting the high temperature polymer electrolyte membrane fuel cells. Graft copolymer strength depending to temperature plays an important role on the degradation of membrane during the operation due that both graft level and mechanical properties of the copolymer should be promising. Graft levels were found to be strongly dependent on the nature of solvents used during grafting. Despite the fact that grafting reactions of 4VP/ETFE performed in cyclohexanone have a highest graft level, DMA indicated that mechanical properties of the resultant copolymers were not favorable. Therefore, *n*-propanol and isopropanol were found to be the most promising solvents to obtain both high graft levels and reasonable mechanical properties to syn-

thesize ETFE-*g*-P4VP copolymers. In the case of NVP grafting, THF is the most promising solvent in terms of both graft level and the strength of graft copolymer. Similarly, both benzyl alcohol and methanol can be regarded as the most favorable solvents for 2VP grafting onto ETFE in the sense of graft level and mechanical properties. DMA results also indicated that grafting resulted in the increase glass transition temperature and stiffness.

SEM-EDAX revealed that copolymers based on 4VP have a much uniform surface depending on graft level. The surface aspects and mechanical properties, taken in conjunction, suggest that although grafting in cyclohexanone yielded more homogeneous copolymer films, their mechanical properties were poor. In the case of NVP and 2VP graft copolymer distribution is not homogenous and graft copolymers tend to gather on one edge.

As conclusion, the resulting graft copolymers are shown to be promising materials for proton exchange membranes. The preparation of membranes by subsequent doping of the promising copolymers described here with phosphoric acid, and characterization of the resultant membranes for high temperature fuel cells are being currently investigated in our group.

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