

Synthesis and characterization of 1H-1,2,4-triazole functional polymer electrolyte membranes (PEMs) based on PVDF and 4-(chloromethyl)styrene via photoinduced grafting

Derya Sasa · Deniz Sinirlioglu · Ali Ekrem Muftuoglu · Fatime Eren · Sevim Unugur Celik · Ayhan Bozkurt

Received: 30 July 2013 / Accepted: 31 October 2013 / Published online: 19 November 2013
© Springer Science+Business Media Dordrecht 2013

Abstract This work exploits a novel photoinduced grafting methodology in the production of 1H-1,2,4-triazole functional anhydrous proton conducting poly(vinylidene fluoride) (PVDF) membranes. High performance of PVDF and design feature of PCMS were combined in a graft copolymer, PVDF-*g*-PCMS, by the polymerization of 4-(chloromethyl)styrene on a PVDF base matrix under UV light. After having been functionalized with 1H-1,2,4-triazole, the polymers were doped with triflic acid (TA) at different stoichiometric ratios with respect to triazole units and the anhydrous polymer electrolyte membranes were prepared. The composition and the structure of polymers were characterized by elemental analysis (EA), ¹H-NMR and FTIR. Their thermal properties were examined by TGA and DSC. TGA demonstrated that the PVDF-*g*-PCMS and PVDF-*g*-PCMS-Tri(TA)_x membranes were thermally stable up to 390 °C and 300 °C, respectively. DSC results illustrated the homogeneity of the materials. According to EA results, 79 % functionalization with 1H-1,2,4-triazole was achieved. Proton conductivity was measured by impedance spectroscopy. PVDF-*g*-PCMS-Tri(TA)₁ with a degree of grafting of 48 % showed a maximum proton conductivity of 0.02 Scm⁻¹ at 150 °C and anhydrous conditions.

Keywords PVDF · 4-(Chloromethyl)styrene · 1H-1,2,4-triazole · Graft copolymers · Photoinduced polymerization · Polymer electrolyte

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been regarded as promising future power supplies with their potential use in transportation vehicles and portable electronic devices owing to their numerous advantages of high energy density, high efficiency, quiet operation and environmental friendliness [1]. The proton exchange membrane (PEM) is a critical constituent in PEMFCs, and serves as an electrolyte that conveys protons between the electrodes and as a partition that prevents mixing of the fuel gases [2, 3]. Perfluorosulfonic acid (PFSA) membranes, such as Nafion (trademark of Du Pont), are at present among the most widely available PEMs and possess good physical and chemical stability and high proton conductivity. However, their high cost is a barrier to the development of high performance fuel cells [4]. Besides, enhanced conductivities can only be attained when the membranes are hydrated. This is a result of proton mobility in the water swollen phase, which persists up to dew point of water [5, 6]. At elevated temperatures, the conductivity tends to decrease due to humidity loss. Hence, it is essential to develop anhydrous proton conducting membranes that are tolerant to hydration and dehydration and allow conduction of protons over non-aqueous phase.

Doping of acidic polymer with heterocyclic protonic solvents such as imidazole, triazole, and tetrazole is a way to get waterfree polymer electrolytes. In such systems, proton transport occurs via “proton hopping”, also known as “Grotthuss mechanism” [3]. 1H-1,2,4-triazole is a potentially useful heterocycle with three nitrogens in the ring. Due to its strong hydrogen bonds 1H-1,2,4-triazole has a relatively high

D. Sasa · D. Sinirlioglu · A. E. Muftuoglu · S. U. Celik · A. Bozkurt
Department of Chemistry, Faculty of Arts and Sciences, Fatih University, Buyukcekmece, Istanbul 34500, Turkey

A. E. Muftuoglu (✉)
Department of Chemical Engineering, Faculty of Chemical and Metallurgical Engineering, Yildiz Technical University, Davutpasa Campus, Esenler, Istanbul 34220, Turkey
e-mail: amuftuoglu@fatih.edu.tr

F. Eren
Department of Chemistry, Faculty of Arts and Sciences, Yildiz Technical University, Davutpasa Campus, Esenler, Istanbul 34220, Turkey

melting point (120 °C). The proton conductivity of pure 1H-1,2,4-triazole is 1.5×10^{-4} S/cm at 115 °C and 1.2×10^{-3} S/cm at its melting point [7]. However, a better approach in the preparation of anhydrous membranes is linking azole moieties covalently to the base polymer. In this manner, leaching problem of the 1H-1,2,4-triazole dopant at elevated temperatures can be eliminated in fuel cell applications. Still, doping with strong acids such as triflic acid and phosphoric acid increases conductivity while efficient operation of the cell is maintained at higher temperatures [8–12]. In poly(vinyl triazole), an azole side-functional polymer, the aliphatic chain improves its fabrication property, and the triazole side groups may act as proton donors and acceptors. The proton transport occurs between hydrogen bonds of neighboring heterocyclic units through structure diffusion [13].

Vinyl or acrylic homo- or co-polymer systems carrying the azole functionalities suffer from weak mechanical strength which has to be overcome for fuel cell application [8–12]. Preparing their blends with high performance polymers may be useful but this route often poses incompatibility problems and result in insufficient mechanical properties due to phase segregation [14–22]. A more elegant approach is the modification of commercially available films by grafting technology using ATRP, gamma irradiation, and ozone pre-treatment methods [23–29].

Asano et al. reported on the development of proton-conducting membranes made by the γ -ray radiation grafting of styrene and its derivatives onto preformed fluorine-containing base films and subsequent sulfonation [30–33]. However, use of these membranes in fuel cell applications would be limited as a result of inferior mechanical properties. These poor mechanical properties were caused by radiation degradation due to high energy γ -ray preirradiation [34]. To avoid degradation of the base film, the same research group employed a novel UV induced polymerization methodology to graft styrene onto a partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE) film and a PTFE film. They obtained stronger membranes with comparable proton conductivities as γ -ray radiation grafted ones and Nafion [35, 36].

Quite recently, we employed the above-mentioned UV induced polymerization process in the grafting of polystyrene onto partially fluorinated poly(vinylidene difluoride) (PVDF) [2]. It was seen that the degree of grafting increased with the grafting time, reaching above 100 % after 8 h while Asano and his coworkers reported about 10 % increase in the degree of grafting of styrene on PTFE films after 8 h [36]. Chen et al. also found that the degree of grafting for ETFE films reached up to 59 % after 6 h of UV irradiation [35]. The high grafting efficiency in our work was partly attributed to the fact that more initiating radicals might have formed on the surface of PVDF due to quantitative homolytic cleavage of C-H bonds rather than sole C-F bonds of PTFE.

It seemed quite probable, therefore, this photografting method would produce high grafting efficiencies when used in conjunction with PVDF and some other styrene monomers. In the present study, 4-(chloromethyl)styrene was grafted on a benzophenone coated PVDF base film in a mixture of acetone and water under UV light. Upon functionalization with 1H-1,2,4-triazole, the polymers were doped with triflic acid (TA) at different stoichiometric ratios with respect to triazole units and the anhydrous polymer electrolyte membranes were obtained.

Experimental

Materials and preparation

Polyvinylidene fluoride (PVDF, average $M_w \sim 534,000$) was purchased from Fluka. The inhibitor in p-chloromethyl styrene (>99 %, Merck) was passed by a basic alumina column and stored at -20 °C. Dimethylformamide (DMF, ≥ 99.9 %), tetrahydrofuran (THF, ≥ 99 %), triethylenamine (TEA) (Merck, ≥ 99 %) and methanol were purchased from Merck. Benzophenone (BP, ≥ 99 %), polyvinyl acetate (PVA, average $M_w \sim 83,000$), 1H-1,2,4-triazole (>98 %) and trifluoromethanesulfonic acid were supplied from Aldrich. They were all reagent grade and used as received.

Preparation of PVDF membranes

The membranes were prepared from 7 % (w/w) PVDF polymer solutions in DMF. The solution was cast on PTFE petri dish to form thin film and dried at room temperature for several hours before heating at 40 °C for 2 h under vacuum. Finally, the polymer was recovered as a flat-sheet membrane from the bottom of the PTFE petri dish². The thickness of the received membranes is in the range of 25–100 μm . All PVDF films were cut into 2 cm \times 2 cm pieces and stored in vacuum at 40 °C before use.

UV photografting of 4-(chloromethyl)styrene to the PVDF films

The UV surface photografting of p-chloromethyl styrene onto the PVDF base film was carried out as follows. First, a 40 μm thick PVDF film was immersed in acetone solution containing 0.5 wt.% benzophenone and 0.5 wt.% poly(vinyl acetate) for 3–5 s at room temperature, and then it was dried under vacuum for 24 h at 40 °C before use. Then, for photografting, 1 mL of 4-(chloromethyl)styrene, 10 mL of distilled water, and 3 mL of acetone were mixed in a quartz tube and nitrogen was bubbled through the solution for about 30 min to remove the oxygen before irradiation. The photosensitizer coated PVDF film was kept standing in a quartz tube containing the 4-(chloromethyl)styrene solution and the quartz tube was

placed into the photoreactor equipped with a 400 W medium pressure mercury lamp (254 nm) to induce grafting. The temperature inside the UV reactor was kept at 60 °C during irradiation [2]. The grafted film was removed and washed with THF for several hours to remove the unreacted monomer and homopolymer. The obtained membrane was then dried in a vacuum oven at 40 °C. Degree of grafting with variation of the UV exposure time was also examined. For this purpose, grafted PVDF films were prepared under the same conditions but with different irradiation times (i.e., 1 h, 2 h, 4 h, 6 h and 8 h).

Modification of PVDF-*g*-PCMS films with triazole and doping with triflic acid

The synthesis of PVDF-*g*-PCMS films with 1H-1,2,4-triazole (Tri) was carried out as depicted in Fig. 1. A stoichiometric amount of Tri and PVDF-*g*-PCMS were dissolved in DMF separately and the solutions were mixed with the addition of 2 mL triethylamine. The reaction mixture was purged with nitrogen and kept at 80 °C for 24 h. The solvent was evaporated and the resulting solid was dried under vacuum. A stoichiometric amount of PVDF-*g*-PCMS-Tri films was admixed with TA in DMF, and homogeneous solutions of PVDF-*g*-PCMS-Tri/TA were produced. Solutions with x (=0.5, 1.0 and 2.0) moles were prepared, where x is the number of moles of triazole per mole of -SO₃H. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates,

and the solvent was evaporated. The films were dried in a vacuum oven for several days at 50 °C.

Characterizations

FT-IR spectra were recorded using a Bruker Alpha-P in ATR in the range of 4,000–400 cm⁻¹. ¹H-NMR spectra were recorded using a 400 MHz Bruker Avance spectrometer. Chemical shifts are reported in ppm relative to TMS as internal standard. Thermal stabilities of the polymer electrolytes were examined by a Perkin Elmer STA 6000 Thermal Analyzer. The samples (~10 mg) were heated from room temperature to 750 °C under N₂ atmosphere at a scanning rate of 10 °C/min. Perkin Elmer JADE Differential Scanning Calorimetry (DSC) was used to investigate the thermal transitions of the samples. The samples (~10 mg) were filled into aluminum pans and then heated to the desired temperature at a rate of 10 °C/min under nitrogen atmosphere. The composition of carbon, hydrogen and nitrogen in the polymers was measured by using Thermo Scientific Flash 2000 Organic Elemental Analyzer. The surface morphology of copolymers was investigated by scanning electron microscopy (SEM), JEOL-7001 FESEM (Tokyo, Japan). All of the samples were coated with gold for 150 s in a sputtering device before SEM measurements.

The graft weight of the films was determined from the increase in weight after grafting, using the following equation:

$$\text{Degree of Grafting} = \frac{W_g - W_o}{W_o} \times 100$$

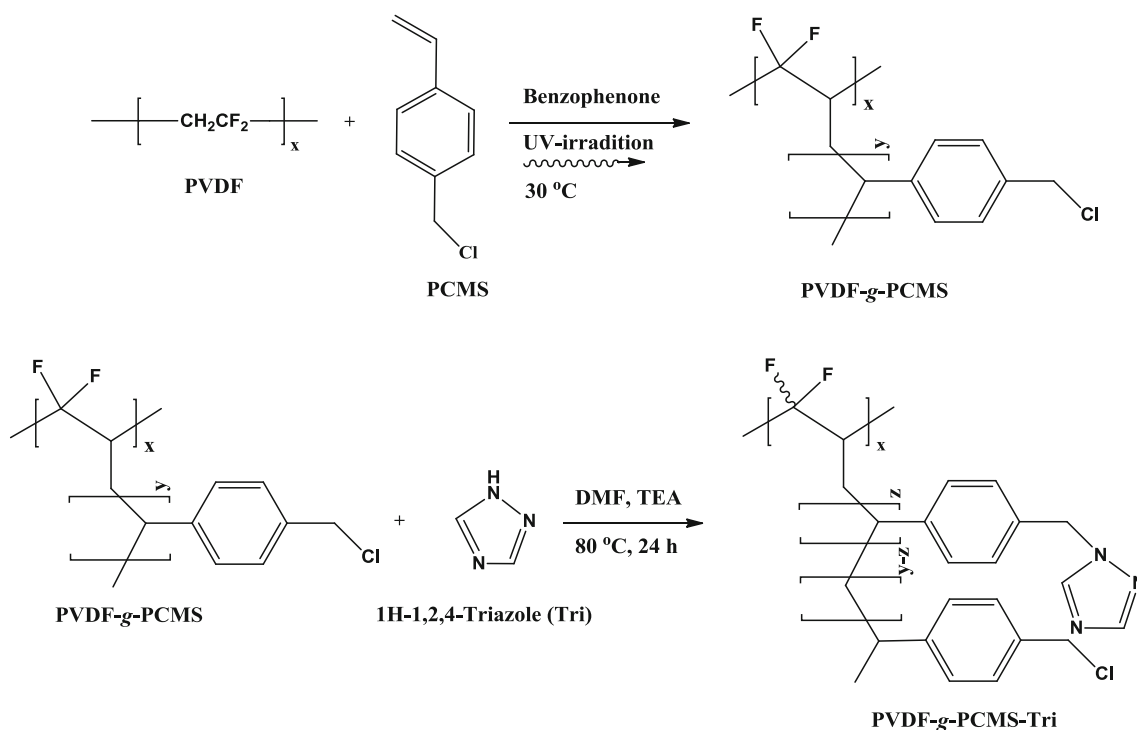


Fig. 1 Synthesis of PVDF-*g*-PCMS-Tri proton conducting membranes by surface photografting

where W_o and W_g are the weights of the film before and after grafting, respectively. The degree of grafting was varied by changing the irradiation time.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The samples were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1 Hz to 3 MHz at 10 °C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between -150 and 250 °C.

Results and discussion

PVDF-*g*-PCMS proton conducting membranes were prepared via irradiation of the cast films coated with sensitizer, followed by modification with 1H-1,2,4-triazole (Tri) as depicted in Fig. 1. Chloromethyl styrene monomers were successfully grafted onto the PVDF films with different degrees of grafting. First, BP sensitizer was coated onto the PVDF films with the use of poly(vinyl acetate) as an adhesion agent. Then, the films were immersed in the chloromethyl styrene solution and exposed to UV irradiation at 30 °C for grafting. During UV irradiation, the coated sensitizer was excited, and macromolecular radicals were generated on the surface of PVDF membranes by abstraction of fluorines or hydrogens. These radicals at the PVDF surfaces initiated the polymerization of chloromethyl styrene. Asano et al., suggested that small amounts of radicals might also be generated inside the PTFE films because of the multiple reflection of UV among the crystalline particles [37]. The grafting in this system seemed to have an interface mechanism, in which grafting started at the layers close to the surface of the film. These grafted layers, which swell in the grafting solution, allowed progressive diffusion of the monomer toward the inner regions of the film. The two grafting interfaces at the two sides of the PVDF film continue to move further into the film interior. Therefore, during grafting, the membrane surface area and thickness both increased, indicating that the grafting proceeded from the surface to the interior of the PVDF films.

The degree of grafting (DG) of chloromethyl styrene on PVDF films were investigated as a function of UV irradiation time, as varied from 0.5 h to 8 h (Table 1). Table 1 lists the

Table 1 Degree of grafting with respect to time

Sample	Graft time (h)	D.G (%)
Memb 1	1	2
Memb 2	2	16
Memb 4	4	48
Memb 6	6	76
Memb 8	8	115

calculated degree of grafting of the corresponding PVDF-*g*-PCMS membranes. It was seen that the degree of grafting increased with the grafting time, reaching above 100 % after 8 h. Asano and his coworkers reported about 10 % increase in the degree of grafting of styrene on PTFE films after 8 h. Chen et al. also found that the degree of grafting for ETFE films reached up to 59 % after 6 h of UV irradiation [38]. The high grafting efficiency in our work as compared to the above-mentioned ones can be partly attributed to the fact that more initiating radicals might have formed on the surface of PVDF due to quantitative homolytic cleavage of C-H bonds rather than sole C-F bonds of PTFE. It is also noteworthy that turbid immiscible mixture at room temperature became transparent indicating that it was miscible at a temperature of 30 °C during irradiation. This probably increased the absorbance of UV radiation by the photosensitizer and, thus, the quantum yield of the photoinitiation.

Elemental analysis

Triazole groups were immobilized by reaction with PVDF-*g*-PCMS. The composition of the polymer was verified by elemental analysis. Triazole contents of the sample were calculated through nitrogen analysis, and the results are summarized in Table 2. It is verified that 1H-1,2,4-triazole are about 79 % accessible to PVDF-*g*-PCMS. Then, a stoichiometric amount of PVDF-*g*-PCMS-Tri films was admixed with TA in DMF, and homogeneous solutions of PVDF-*g*-PCMS-Tri:TA were produced. Solutions with ($x=0.5, 1.0$ and 2.0) moles were prepared, where x is the number of moles of triazole per mole of TA. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was evaporated and dried in vacuum oven for several days at 50 °C (Fig. 2).

¹H NMR analysis

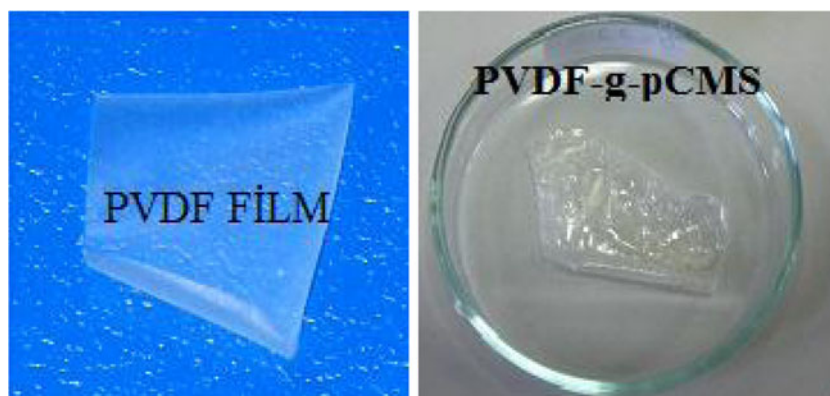
The successful graft copolymerization was confirmed using ¹H-NMR spectroscopy. ¹H-NMR spectra for PVDF and PVDF-*g*-PCMS (Memb 4) were presented in Fig. 3. For both samples, the peaks of solvent (DMSO) and water appeared at 2.51 and 3.40 ppm, respectively. The ¹H-NMR spectrum exhibited the characteristic multiplets centered at 2.9 and 2.3 ppm originating from the methylene groups in -CH₂-

Table 2 Azole content of Tri calculated from elemental analysis results

Sample	C (%)	H (%)	N (%)	Azole (%) ^a	
PVDF- <i>g</i> -PCMS-Tri	65.51	7.22	14.32	100	Calculated
PVDF- <i>g</i> -PCMS-Tri	62.93	7.35	11.39	79	Found

^a On a % by weight basis

Fig. 2 Free standing films of PVDF and PVDF-*g*-PCMS



CF₂-CH₂-CF₂-CH₂-CF₂- and -CF₂-CH₂-CH₂-CF₂- sequences appearing in the normal tail-to-head and reversed tail-to-tail VDF additions [2]. The spectrum of the PVDF-*g*-PCMS graft copolymers exhibited additional signals located in the 1.8–2.2 ppm and 7.3–6.5 ppm ranges assigned to methylene and methyne groups of poly(chloromethyl styrene) and to the aromatic protons, respectively. After modification of PVDF-*g*-PCMS with triazole, the appearance of the peak belonging to -CH proton of the triazole ring at 8.12 ppm is a typical indication for the successful completion of modification reaction. Also, the signals at 8.12 (g,h) ppm and 4.82–4.60 (f) ppm are assigned to the methine proton and the methylene protons adjacent to the triazole ring, respectively. And 7.6–6.8 ppm ranges assigned to methyne groups of the aromatic protons [9]. ¹H-NMR spectra confirmed the elemental analysis results and ¹H-NMR spectra shows the successful completion of modification reaction. From the ¹H-NMR spectrum, the integration ratio of the protons confirmed the modification of PVDF-*g*-PCMS with triazole as depicted in Fig. 3.

FT-IR analysis

Infrared spectroscopy was employed to provide information about the chemical structure of the unmodified and modified PVDF membranes. Figure 4 shows the FT-IR spectra of the PVDF base film, graft membrane (Memb 4), modified with triazole proton conducting membrane (Memb 4-Tri) and triflic acid doped proton conducting membranes. The asymmetric and symmetric stretching vibrations of the CH₂ group in the PVDF base film (Fig. 4a) were located, respectively, at 3,024 cm⁻¹ and 2,982 cm⁻¹. The strong peak which appeared at 1,404 cm⁻¹ corresponds to CH₂ stretching vibrations. Strong and wide peaks appearing between 1,246 and 1,070 cm⁻¹ correspond to the C-F stretching and were characteristic peaks of the PVDF base film. For the chloromethylstyrene grafted PVDF membranes the presence of the benzene rings in the graft chains was confirmed by the =C-H stretching vibration at 3,027 cm⁻¹ and the skeletal C=C stretching vibration at 1,496 and 1,602 cm⁻¹.

The monosubstitution of the benzene ring was confirmed by the two bands of C-H aromatic out-of-plane deformation at 821 cm⁻¹ and 665 cm⁻¹. These signs confirmed that the monomers were grafted onto the PVDF base films (Fig. 4b). The FT-IR spectra of PVDF-*g*-PCMS-Tri proton conducting membranes (Memb 4-Tri) are given in Fig. 4c. Memb 4-Tri exhibited a medium absorption at 1,650 cm⁻¹ and 1,450 cm⁻¹ due to C=N and C-N stretching of the triazole ring. Additionally, the peak which appears at between 3,600 and 3,100 cm⁻¹ shows the N-H absorption. Fig. 4d, e, and f show the FTIR spectra of acid-doped PVDF-PCMS-Tri. Triflic acid gives several absorptions between 1,000 cm⁻¹ and 1,250 cm⁻¹. The strong bands at 1,208 and 1,269 cm⁻¹ are attributed to SO₂, and a strong absorption peak at 1,026 cm⁻¹ most probably belongs to -SO₃⁻[H⁺]. The formation of a peak at around 3,170 cm⁻¹ shows the protonation of the triazole rings [9], in addition to the broad peaks around 3,500 cm⁻¹.

Thermal analysis

The thermal stabilities of base PVDF and PVDF graft membranes (Memb 4), PVDF-*g*-PCMS-Tri and proton conducting membranes (PVDF-*g*-PCMS-TriTA; x=0.5, 1 and 2) were investigated by TGA as shown in Fig. 5. The base PVDF showed excellent thermal stability up to 440 °C. The TGA curves of PVDF-*g*-PCMS polymer exhibited a satisfactory thermal stability up to 390 °C. 40 % of PVDF-*g*-PCMS polymer decomposes between 390 and 440 °C because of degradation of benzene rings and also polymer main chain, after 440 °C, second weight loss region occurs because of degradation of PVDF. After modification of PVDF-*g*-PCMS with triazole, the first slight weight loss of proton conducting membrane was observed around 100 °C, which is mostly attributable to the loss of adsorbed water by membrane. The second weight loss took between 190 °C and 375 °C owing to the existence of degradation of triazole units and polymer backbone after 380 °C, third weight loss region occurs because of decomposition of the copolymer backbone and PVDF [2, 9].

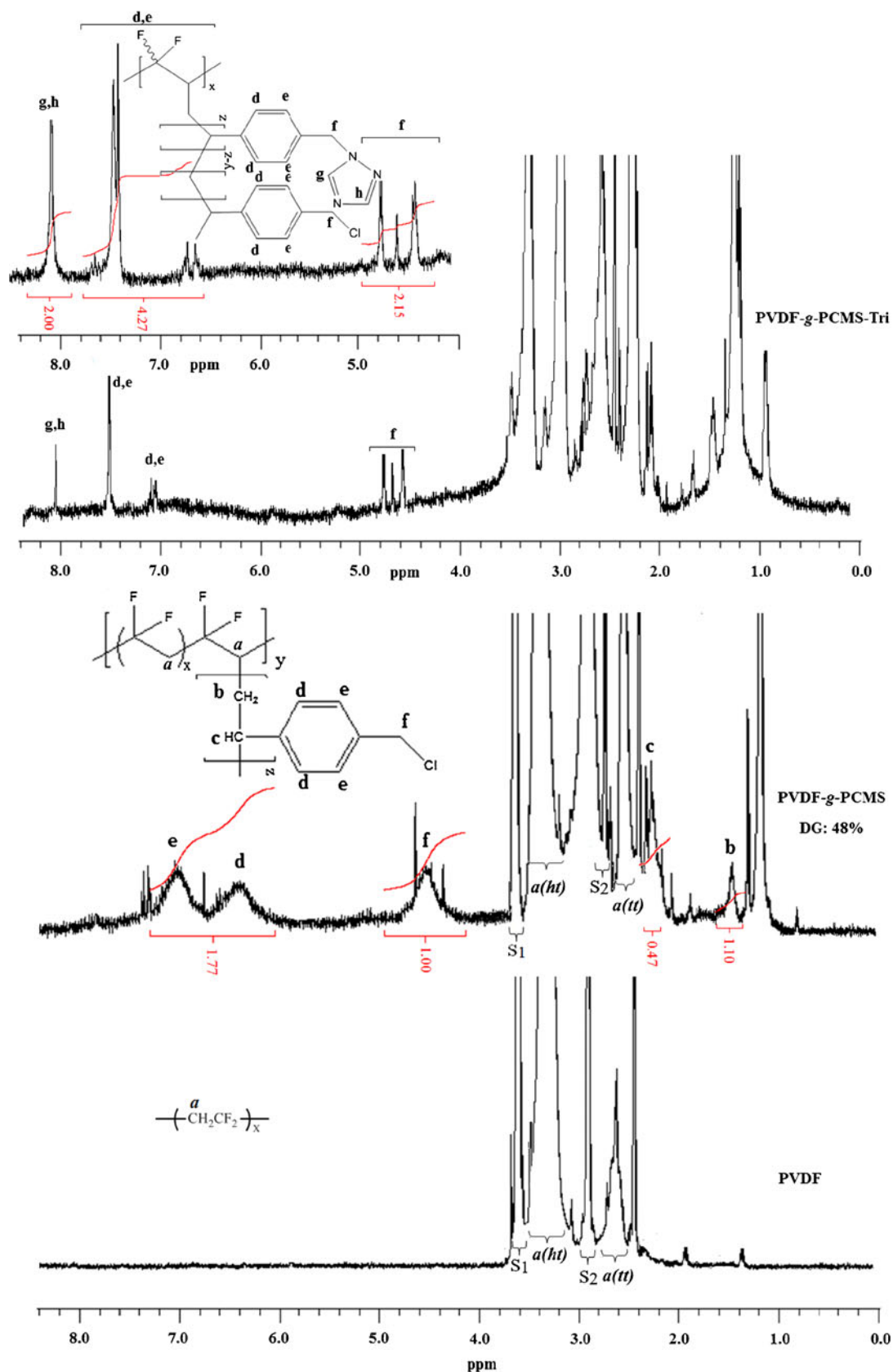


Fig. 3 ¹H-NMR spectra of PVDF, PVDF-g-PCMS (Memb 4) and PVDF-g-PCMS-Tri recorded in d⁶-DMSO

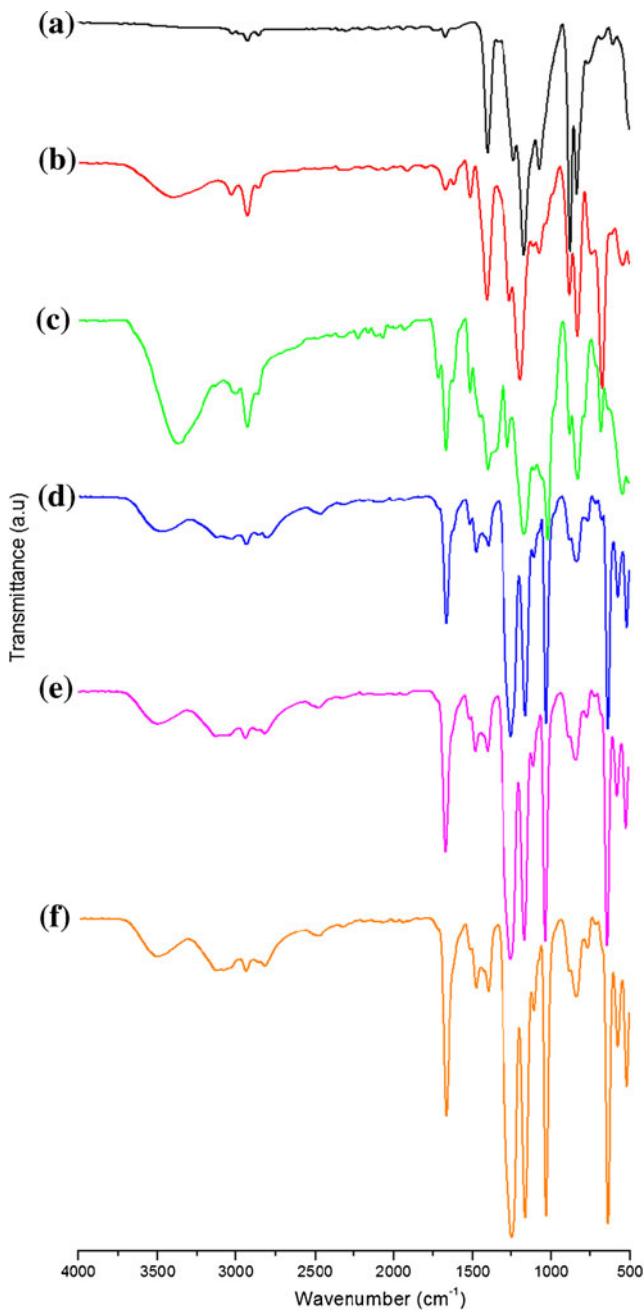


Fig. 4 FTIR spectra of **a** PVDF, **b** PVDF-*g*-PCMS, **c** PVDF-*g*-PCMS-Tri, **d** PVDF-*g*-PCMS-Tri0.5TA, **e** PVDF-*g*-PCMS-Tri1TA and **f** PVDF-*g*-PCMS-Tri2TA

After doping the PVDF-*g*-PCMS-Tri functional membranes with triflic acid, the thermal stability of membranes increased. The highest thermal stability belongs to PVDF-*g*-PCMS-Tri2TA (300 °C) and the other membranes (PVDF-*g*-PCMS-Tri-*x*TA; *x*=0.5 and 1.0) are thermally stable up to approximately 270 °C. For all acid doped samples, there is a little decomposition (10 % of the samples) between 270 and 300 °C and major weight loss occurs between 300 and 430 °C which presumably derives from the decomposition of the polymer electrolyte main chain and PVDF backbone. In

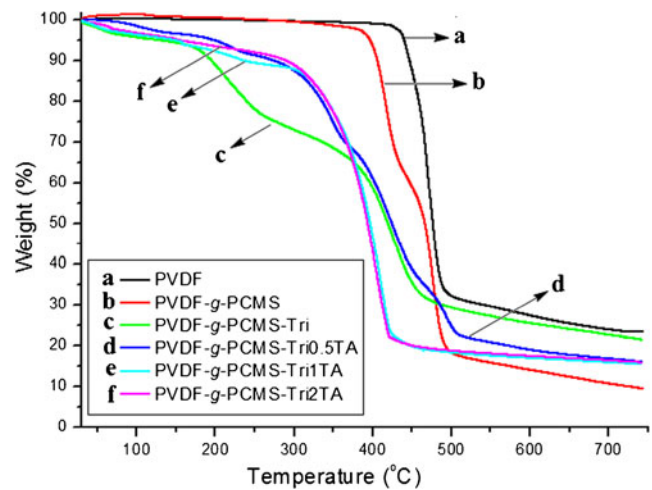


Fig. 5 TG thermograms of **a** PVDF, **b** PVDF-*g*-PCMS, **c** PVDF-*g*-PCMS-Tri, **d** PVDF-*g*-PCMS-Tri0.5TA, **e** PVDF-*g*-PCMS-Tri1TA and **f** PVDF-*g*-PCMS-Tri2TA polymers at a heating rate of 10 °C/min in inert atmosphere

addition, in these acid doped samples, the weight loss begins at higher temperatures compared with triazole functional membrane (PVDF-*g*-PCMS-Tri) as nearly single step. This may be due to the hydrogen bonding between triflic acid and triazole units, which hinders the triazole unit degradation [9].

In DSC measurements, the second heating curves were evaluated. Previously, the T_g of pure PCMS was reported as 95 °C [9]. T_g of PVDF was observed at -50 °C [39] and PVDF-*g*-PCMS exhibits a glass transition at approximately 110 °C and melting point (T_m) was observed at approximately 155 °C. Since the photografting was applied on the membrane

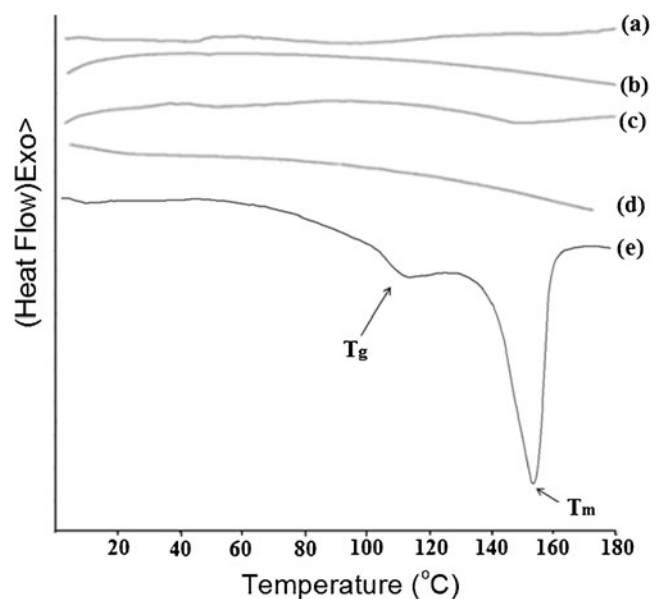
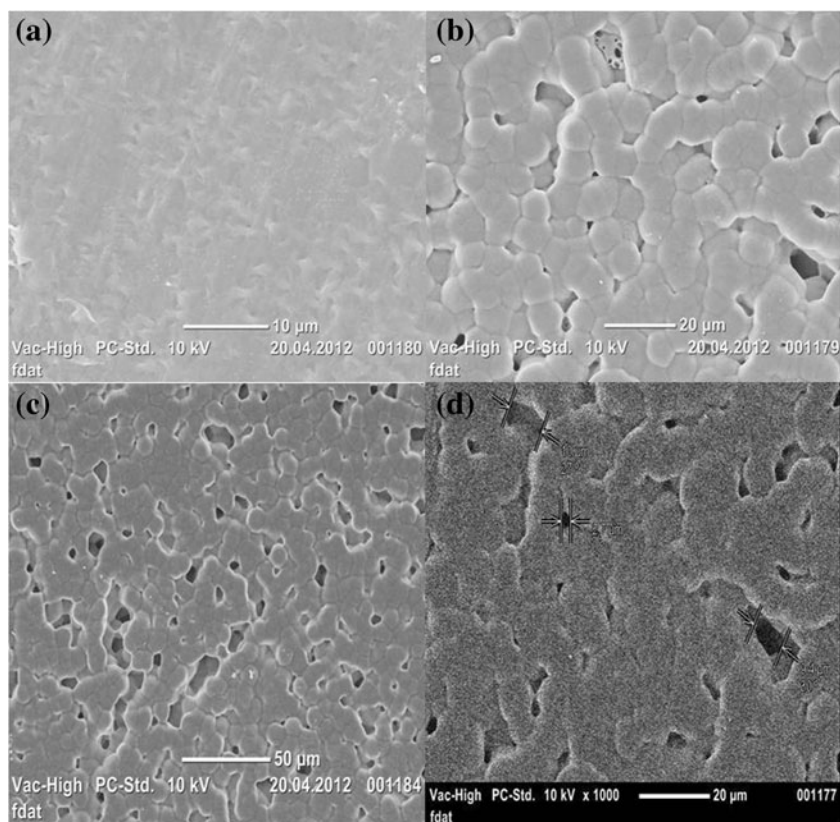


Fig. 6 DSC thermograms of **a** PVDF-*g*-PCMS-Tri0.5TA, **b** PVDF-*g*-PCMS-Tri1TA, **c** PVDF-*g*-PCMS-Tri, **d** PVDF-*g*-PCMS-Tri2TA and **e** PVDF-*g*-PCMS recorded under N₂ atmosphere at a heating rate of 10 °C/min

Fig. 7 SEM images of the surface of **a** virgin PVDF, 10 μm and PVDF-*g*-PCMS polymer at different micrometer-scale level, **b** 20 μm , **c** 50 μm and **(d)** 20 μm , respectively



form of PVDF, the T_m was observed due to the presence of ordered PVDF regions. For PVDF-*g*-PCMS-Tri there is a glass transition temperature of 135 $^{\circ}\text{C}$, but T_m was not observed since modification is done in solution and the ordered parts of PVDF may be destroyed with triazole modification (Fig. 6). The T_g of PVDF-*g*-PCMS-Tri0.5TA, PVDF-*g*-PCMS-Tri1TA and PVDF-*g*-PCMS-Tri2TA are not obvious which may be due to ionic interactions between acid and base units.

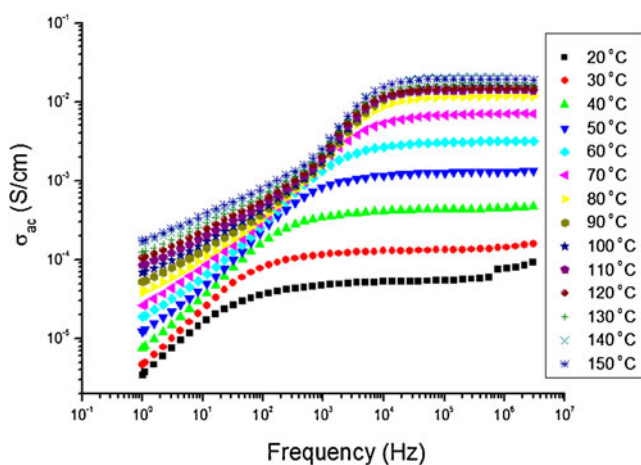


Fig. 8 AC conductivity versus frequency of PVDF-*g*-PCMS-Tri1TA at several temperatures

Morphology

Surface morphologies of the virgin PVDF membrane and PVDF-*g*-PCMS membranes were investigated by scanning electron microscopy (SEM). There are some small hollows on the surface of the PVDF membrane as depicted in Fig. 7(a). The hollows are filled with poly(chloromethylstyrene) as

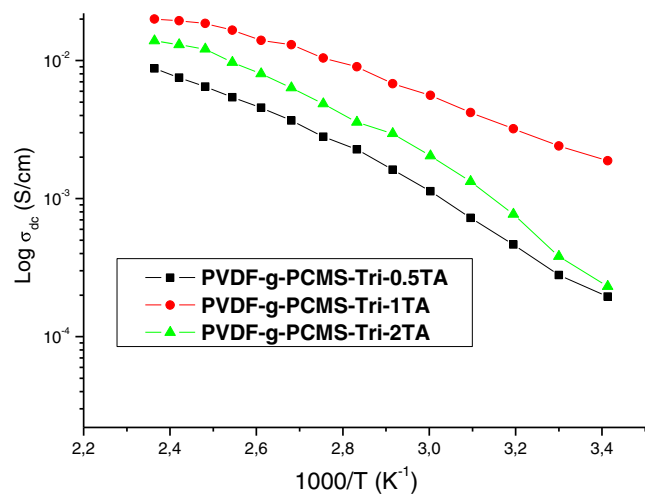


Fig. 9 Variation of the DC proton conductivity of triflic acid (TA) doped PVDF-*g*-PCMS-Tri polymers as a function of reciprocal temperature

Table 3 Doping ratio with triflic acid, T_g and maximum proton conductivity values of PVDF based membranes

Sample name	Doping ratio with (TA)	T _g (°C)	Max. proton conductivity (Scm ⁻¹)
PVDF	–	–50 °C	–
PVDF- <i>g</i> -PCMS	–	110 °C	–
PVDF- <i>g</i> -PCMS-Tri	–	^a	–
PVDF- <i>g</i> -PCMS-Tri0.5TA	1:0.5	^a	0.009 Scm ⁻¹ at 150 °C
PVDF- <i>g</i> -PCMS-Tri1TA	1:1	^a	0.02 Scm ⁻¹ at 150 °C
PVDF- <i>g</i> -PCMS-Tri2TA	1:2	^a	0.012 Scm ⁻¹ at 120 °C

^aT_g was not observed due to hydrogen bonding network formation, and ionic interactions may result in the restriction of the segmental relaxations

shown in Fig. 7(b, c, d), which indicates that chloromethyl styrene (CMS) is grafted into the virgin PVDF at different micro-meter scales. After CMS monomer has been grafted on the surface of PVDF, especially images (b, c, d) show some hollows due to the solvent evaporation during the membrane preparation [40, 41].

Proton conductivity

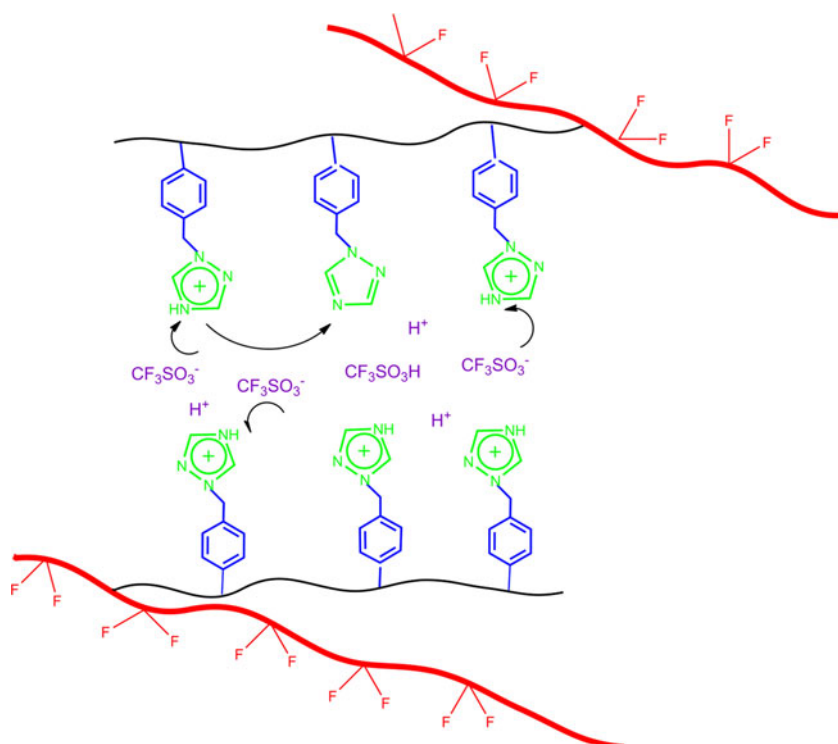
Proton conductivity is one of the most important properties of polymer electrolyte membranes for fuel cells. The AC conductivities, σ_{ac}(ω) of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities (σ_{ac}(ω)) were measured using following equation:

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \epsilon''(\omega)\omega\epsilon_0$$

where σ'(ω) is the real part of conductivity, ω=2πf is the angular frequency, ε₀ is the vacuum permittivity (ε₀=8.852×10⁻¹⁴ F/cm), and ε'' is the imaginary part of complex dielectric permittivity (ε*). The proton conductivities of anhydrous nanocomposite polymer electrolytes were measured from 20 °C to 150 °C. Figure 8 shows the AC conductivity of PVDF-*g*-PCMS-Tri1TA versus frequency at several temperatures. As expected the proton conductivity increases as temperature increases.

The DC conductivity (σ_{dc}) of the samples was derived from the plateaus of log σ_{ac} versus log F by linear fitting of the data. The DC conductivities of the samples were compared in Fig. 9. The conductivity isotherm illustrates that the DC conductivity depends on the temperature and doping ratio of triflic acid. In the anhydrous conditions, the proton conductivity of PVDF-*g*-PCMS-Tri1TA was measured as 0.02 Scm⁻¹ at 150 °C (Table 3). The DC curves are closer to linear

Fig. 10 Possible mechanism of proton transport in PVDF-*g*-PCMS-Tri-(TA)_x (x=0.5, 1.0 and 2.0) membranes



type curves which can be explained with Arrhenius equation:

$$\ln \sigma = \ln \sigma_0 - E_a/kT$$

where σ_0 is the pre-exponential terms, E_a is the activation energy, and k is the Boltzmann constant. Arrhenius behavior is generally observed in the matrices where during the measurement temperature range no T_g was observed and there is no change in linearity of DC curve. Here it can be said that the segmental motions have little contribution to the conductivity. In that grafted matrix the proton conductivity is carried out between triazole and triflic acid units. Since the triazole attachment and doping were performed in homogeneous solution medium we can consider a matrix with hydrophobic PVDF backbone and a channel that has triazole units interacting with triflic acid molecules (Fig. 10). Here the acid ratio is not very high and we do not expect a Vehicular type proton conductivity but a Grotthous mechanism is proposed in that matrix.

PVDF has a similar backbone with Nafion and since it is cheaper the scientist tried to mimic the matrix of Nafion by grafting sulfonic acid groups into PVDF via photografting [2], irradiation [42] or ATRP methods [43]. The proton conductivity in these studies is based on the humidity content and not applicable at high temperatures. In this study proton conduction is based on the azole and acid units and the material can be used at high temperatures. The grafted structure PCMS-Tri was previously studied and high proton conductivity was reported (0.042 S/cm) [9]. In this study PVDF provided a high thermally and mechanically stable matrix and good film formability. Possible mechanism of proton transport in PVDF-g-PCMS-Tri-(TA)_x, in which triflic acid is coordinated with triazole groups is tentatively depicted in Fig. 10.

Conclusions

Proton exchange membranes were prepared by UV photoinduced surface grafting of 4-(chloromethyl)styrene onto poly(vinylidene fluoride) followed by a modification with 1H-1,2,4-triazole. The degrees of grafting in PVDF-g-PCMS films obtained by surface grafting increased with irradiation time, reaching above 100 % after 8 h (115 %). The success of graft copolymerization was confirmed using ¹H-NMR and FT-IR. The modification of graft copolymer with triazole was verified by elemental analysis, FT-IR and ¹H-NMR spectroscopies. Thermal properties were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. TGA showed that the PVDF-g-PCMS and PVDF-g-PCMS-Tri(TA)_x membranes (x=0.5, 1.0 and 2.0) are thermally stable up 390 °C and ~300 °C, respectively. DSC results illustrated the homogeneity of the materials. The

proton conductivity of the membranes was investigated for PVDF-g-PCMS-Tri(TA) (x=0.5, 1.0 and 2.0) membranes. Under anhydrous conditions, PVDF-g-PCMS-Tri(TA) with a degree of grafting of 48 % showed a maximum proton conductivity of approximately 0.02 Scm⁻¹ at 150 °C.

Acknowledgments We would like to thank Fatih University-BINATAM center for the SEM measurements. This work was supported by the Scientific Research Fund of Fatih University under the project number P50021201_B.

References

- Matsumoto K, Higashihara T, Ueda M (2009) *Macromolecules* 42: 1161–1166
- Golcuk S, Muftuoglu AE, Celik SU, Bozkurt A (2013) *J Polym Res* 20(5):144
- Celik SU, Bozkurt A, Hosseini SS (2012) *Prog Polym Sci Progress* 37:1265–1291
- Li L, Deng B, Ji Y, Yu Y, Xie L, Li J, Lu X (2010) *J Membr Sci* 346: 113–120
- Schuster ME, Meyer WH (2003) *Annu Rev Mater Res* 33:233–261
- Kreuer KD (2001) *J Membr Sci* 185(1):29–39
- Li S, Zhou Z, Zhang Y, Liu M (2005) *Chem Mater* 17:5884–5886
- Celik SU, Bozkurt A (2013) *J Polym Res* 20:63
- Ozden S, Celik SU, Bozkurt A (2010) *J Polym Sci Part A Polym Chem* 48:4974–4980
- Ozden S, Celik SU, Bozkurt A (2010) *Electrochim Acta* 55:8498–8503
- Aslan A, Celik SU, Sen U, Haser R, Bozkurt A (2009) *Electrochim Acta* 54:2957–2961
- Celik SU, Bozkurt A (2008) *Eur Polym J* 44:213–218
- Pu H, Ye S, Wan D (2007) *Electrochim Acta* 52:5879–5883
- Gustian I, Celik SU, Bozkurt A (2012) *J Mater Res* 27(20):2650–2656
- Hazarika M, Jana T (2012) *Appl Mater Interfaces* 4:5256–5265
- Yamada M, Honma I (2005) *Polymer* 46:2986–2992
- Gunday ST, Bozkurt A, Meyer WH, Wegner G (2006) *J Polym Sci Part B Polym Phys* 44:3315–3322
- Sen U, Bozkurt A, Ata A (2010) *J Power Sources* 195:7720–7726
- Sen U, Bozkurt A, Ata A (2011) *J Appl Polym Sci* 120:1193–1198
- Sen U, Celik SU, Ata A, Bozkurt A (2008) *Int J Hydrog Energy* 33: 2808–2815
- Aslan A, Bozkurt A (2009) *J Power Sources* 191:442–447
- Kim JD, Mori T, Hayashi S, Honma I (2007) *J Electrochem Soc* 154: A290–A294
- Sui Y, Wang Z, Gao X, Gao C (2012) *J Membr Sci* 413:38–47
- Xu FJ, Neoh KG, Kang ET (2009) *Prog Polym Sci* 34:719–761
- Liu H, Yang S, Wang S, Fang J, Jiang L, Sun G (2011) *J Membr Sci* 369:277–283
- Fei G, Shin J, Kang SA, Ko BS, Kang PH, Lee YS, Nho YC (2010) *J Polym Sci Part A Polym Chem* 48:563–569
- Sherazi TA, Ahmad S, Kashmiri MA, Guiver MD (2008) *J Membr Sci* 325:964–972
- Hasegawa S, Takahashi S, Iwase H, Koizumi S, Morishita N, Sato K, Narita T, Ohnuma M, Maekawa Y (2011) *Polymer* 52:98–106
- Fei G, Kang SA (2010) *J Appl Polym Sci* 117:2380–2385
- Chen J, Asano M, Yamaki T, Yoshida M (2005) *J Membr Sci* 256: 38–45
- Chen J, Asano M, Maekawa Y, Yoshida M (2006) *J Membr Sci* 277: 249–257

32. Chen J, Asano M, Yamaki T, Yoshida M (2006) *J Membr Sci* 269: 194–204
33. Chen J, Asano M, Yamaki T, Yoshida M (2006) *J Power Sources* 158: 69–77
34. Fayolle B, Audouin L, Verdu J (2003) *Polymer* 44:2773–2780
35. Chen J, Asano M, Maekawa Y, Sakamura T, Kubota H, Yoshida M (2006) *Electrochem Solid-State Lett* 9:G184–G186
36. Asano M, Chen J, Maekawa Y, Sakamura T, Kubota H, Yoshida M (2007) *J Polym Sci Part A Polym Chem* 45:2624–2637
37. Septiani U, Chen J, Asano M, Maekawa Y, Yoshida M, Kubota H (2007) *J Mater Sci* 42:1330–1335
38. Qiu J, Zhang J, Chen J, Peng J, Xu L, Zhai M, Li J, Wei G (2009) *J Membr Sci* 334:9–15
39. Tang W, Zhu T, Zhou P, Zhao W, Wang Q, Feng G, Yuan H (2011) *J Mater Sci* 46:6656–6663
40. Slade RCT, Varcoe JR (2005) *Solid State Ionics* 176:585–597
41. Choi JH, Gwon SJ, Shon JY, Jung CH, Ihm YH, Lim YM, Nho YC (2008) *J Ind Eng Chem* 14:116–119
42. Abdel-Hady EE, El-Toony MM, Abdel-Hamed MO (2013) *Electrochim Acta* 103:32–37
43. Kim YW, Choi JK, Park JT, Kim JH (2008) *J Membr Sci* 313:315–322