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ORIGINAL PAPER

An investigation of proton conductivity of PVDF based 5-aminotetrazole functional polymer electrolyte membranes (PEMs) prepared via direct surface-initiated AGET ATRP of glycidyl methacrylate (GMA)

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Abstract High performance of PVDF and design feature of glycidyl methacrylate (GMA) were combined in a graft copolymer with a goal of being used in fuel cells. PVDF-*g*-PGMA was obtained via atom transfer radical polymerization (ATRP) of GMA on a PVDF matrix using a “grafting from” approach. Specifically, AGET (activators generated by electron transfer) ATRP was employed in the surface grafting, which produced acceptable grafting degrees. Synthesized PVDF-*g*-PGMA copolymer was modified with 5-aminotetrazole and doped with triflic acid (TA) at different mole ratios with respect to aminotetrazole units, eventually fabricating various PVDF-*g*-PGMA-ATet-(TA)x membranes. The composition and the structure of polymers were characterized by Energy Dispersive X-ray spectroscopy (EDS), ^{1}H-NMR and FTIR. Their thermal properties were examined by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA demonstrated that the PVDF-*g*-PGMA and PVDF-*g*-PGMA-ATet-(TA)x membranes were thermally stable up to 275 °C, 200 °C (x=2.0) and 230 °C (x=4.0). According to EDS results, 71.35 % functionalization with 5-aminotetrazole was achieved. PVDF-*g*-PGMA-ATet-(TA)$_4$ showed a maximum proton conductivity of 0.011 Scm^{-1} at 150 °C and anhydrous conditions.

Keywords PVDF · AGET ATRP · Glycidyl methacrylate · 5-aminotetrazole · Surface grafting · Polymer electrolyte membrane

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have recently attracted much attention as alternative energy sources for various applications such as transportation vehicles and portable electronic devices [1–10]. The proton exchange membrane (PEM) is a critical component in PEMFCs, and plays a significant role as an electrolyte in transporting protons between the electrodes and as a barrier in the prevention of mixing of the fuel gases [2, 5, 9, 10]. For decades, the representative proton conducting polymer electrolyte membranes have been perfluorosulfonic acid (PFSA) polymers, such as Nafion from Du Pont, which have excellent electrochemical, mechanical and thermal properties and provide high proton conductivity in the fully hydrated state [9, 10]. However, their high cost is an obstacle to the development of high performance fuel cells [11]. Furthermore, the performance of Nafion decreases dramatically at high temperature due to drying, which limits its use in PEMFC applications [12, 13]. Therefore, there is an enormous need for polymer

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electrolyte membranes having low cost and showing high performance under anhydrous conditions at high temperatures (>120 °C) [2, 5, 8, 9, 12]

Anhydrous PEMs have been prepared by doping acidic polymers with heterocyclic protonic solvents such as imidazole, triazole, and tetrazole. In such membranes, "proton hopping", also known as "Grotthuss mechanism" is the controlling step for proton transport [9, 14]. 5-Aminotetrazole (ATet) is one of the most promising heterocycles because it has a high melting point (203 °C) and is a crystalline solid at room temperature, which makes it easy to handle. Additionally, ATet contains four nitrogen atoms in the ring which provides more sites for proton transfer [9]. An alternate approach in the production of anhydrous membranes is tethering azole moieties covalently to the base polymer. In this way, leaching out problem of the 5-Aminotetrazole (ATet) dopant at high temperatures can be eliminated in fuel cell applications. In these membranes, conductivity may be increased being doped with strong acids such as triflic acid and phosphoric acid while efficient operation of the cell is maintained at elevated temperatures [9, 15, 16].

An elegant approach in the fabrication of PEMs with improved mechanical properties is the modification of commercially available films by grafting technology using UV light [2, 8, 17], gamma and X-ray irradiation [18–22], and atom transfer radical polymerization (ATRP) [7, 23–37] methods. Employing poly(vinylidene fluoride) (PVDF) as the base film has advantages such as low cost, high chemical resistance, enhanced thermal and mechanical properties [8, 20]. So far, surface modification of PVDF films has been studied for several applications. However, there are a number of studies about its usage as proton conducting membranes [25–31] and only few studies related with anhydrous PEMs [2, 8]. Previously, we reported a UV induced polymerization process in the grafting of polystyrene and poly(4-chloromethyl)styrene onto partially fluorinated poly(vinylidene difluoride) (PVDF) [2, 8]. Recently, use of ATRP has become favourable in the modification of fluoropolymer membranes to obtain PEMs [25–31] due to its tolerance for impurities and functional groups besides mild polymerization conditions. But in most cases, ATRP involves organic solvents, high temperatures, and multi-step strategies, which is inevitable for membranes lacking active groups. However, the possibility of direct initiation from PVDF surface in ATRP has been shown without the need for surface linking initiator moieties [32–34]. Furthermore, employing AGET (activators generated by electron transfer) ATRP, which is a new ATRP initiating system developed to facilitate solution ATRP in aqueous media, use of organic solvents can be greatly avoided [30, 38]. In this system, a reducing agent is used to react with Cu (II) complex and to generate the activator instead of adding Cu (I) complex at the start.

Glycidyl methacrylate (GMA) is a useful monomer because the epoxy group can undergo ring opening reactions with various compounds. For this reason, polymers with epoxy groups can offer numerous functionalization possibilities. Previously, Celik et al. studied polyglycidyl methacrylate (PGMA)-based polymer electrolyte membranes through immobilization of aminotetrazole (ATet), followed by subsequent doping with triflic and phosphoric acid and reported a maximum proton conductivity of 0.01 S/cm at 150 °C for PGMA-ATet-4H_3PO_4 [14]. There are also studies concerning ATRP of GMA to obtain polymer electrolytes [7, 28, 29, 31]. Although reports dealing with ATRP of several monomers in the grafting on PVDF are available [7, 28–31, 38, 39], to the best of our knowledge, this study is the first to describe direct surface-initiated ATRP of GMA in the preparation of PVDF-*g*-PGMA graft copolymers and PVDF-*g*-PGMA-ATet anhydrous membranes.

In this contribution, a facile PVDF membrane modification method was put forward based on AGET-ATRP directly initiated from membrane surface at room temperature. Ascorbic acid (AscA) was used as the reducing agent to reduce the air stable Cu (II) complex, $CuCl_2$- *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA), resulting in the generation of an active catalyst. Glycidyl methacrylate (GMA) monomer was grafted directly from PVDF membrane surface. The synthesis of PGMA on the PVDF membrane by AGET-ATRP was represented in Fig. 1. PVDF-*g*-PGMA graft membranes were then quantitatively modified with 5-aminotetrazole to achieve PVDF-*g*-PGMA-ATet by ring opening of the epoxide group. The chemical composition of the modified PVDF surfaces was determined by Energy Dispersive X-ray spectroscopy (EDS). Their thermal properties were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) measurements. The proton conductivity of the membranes was investigated with impedance analyzer for PVDF-*g*-PGMA-ATet-(TA)x (x=1.0, 2.0 and 4.0) membranes.

Experimental

Materials and preparation

Polyvinylidene fluoride (PVDF, average Mw~534,000) was purchased from Fluka. Glycidyl methacrylate (>99 %, Merck) was passed through basic alumina column to remove the inhibitor and stored at −20 °C. *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich), Dimethylformamide (DMF, ≥99.9 %), $CuCl_2$ (≥99.99 %, Aldrich), ascorbic acid (AscA, 99 %, (Sigma)), methanol (99.9 %, Aldrich), chloroform (99 %, Merck), 5-aminotetrazole (97 %, Aldrich) and trifluoromethanesulfonic acid (Alfa Aesar, 98 %) were used as received.

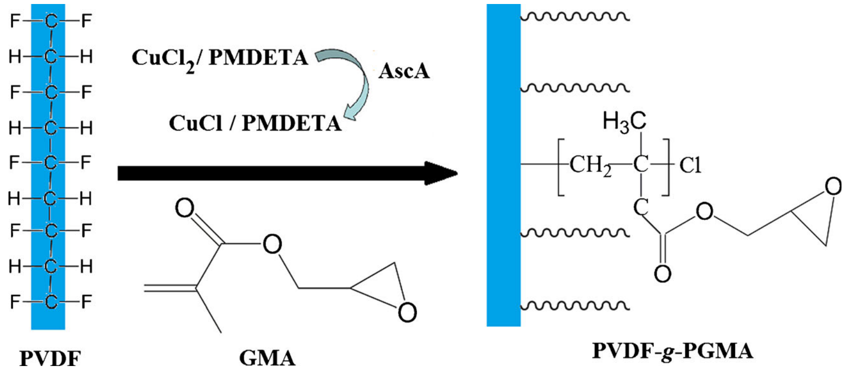

Fig. 1 Schematic representation of the AGET-ATRP of GMA directly initiated from the PVDF membrane surface

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 dish. The thickness of the received membranes is in the range of 25–100 μm. All PVDF films were cut into 2 cm×2 cm pieces and stored in vacuum at 40 °C before use.

The AGET-ATRP of GMA

A typical procedure is given as following for GMA: the rinsed and dried PVDF membrane was soaked in 30 mL methanol for 1 min to wet out and introduced into a flask of 100 mL. Then, GMA (4 mL, 30 mmol), CuCl$_2$ (39 μg, 0.22 mmol), PMDETA (27 μL, 0.13 mmol), and 20 mL of water were added sequentially. Nitrogen gas was bubbled through the reaction mixture for 10 min while stirring. After that, AscA 24 μg (0.04 mmol) was added to the flask to reduce the Cu (II) complex to the activator Cu (I) complex and start the polymerization at room temperature. After a predetermined time (24 h), the polymerization was stopped by exposing the solution to air. Then, the membrane was washed in chloroform at 40 °C for 2 h to remove PGMA homopolymer.

Modification of PVDF-*g*-PGMA membrane with 5-aminotetrazole and doping with triflic acid

The synthesis of PVDF-*g*-PGMA films with 5-aminotetrazole (ATet) was carried out as depicted in Fig. 2. PVDF-*g*-PGMA was dissolved in DMF at 60 °C for 48 h, 5-amino-tetrazole monohydrate (ATet) was added into the solution with molar stoichiometric ratio of 1:5 (GMA:tetrazole) [14]. The reaction mixture was purged with nitrogen and the temperature was set to 100 °C and solution was stirred for 20 h, then the solution

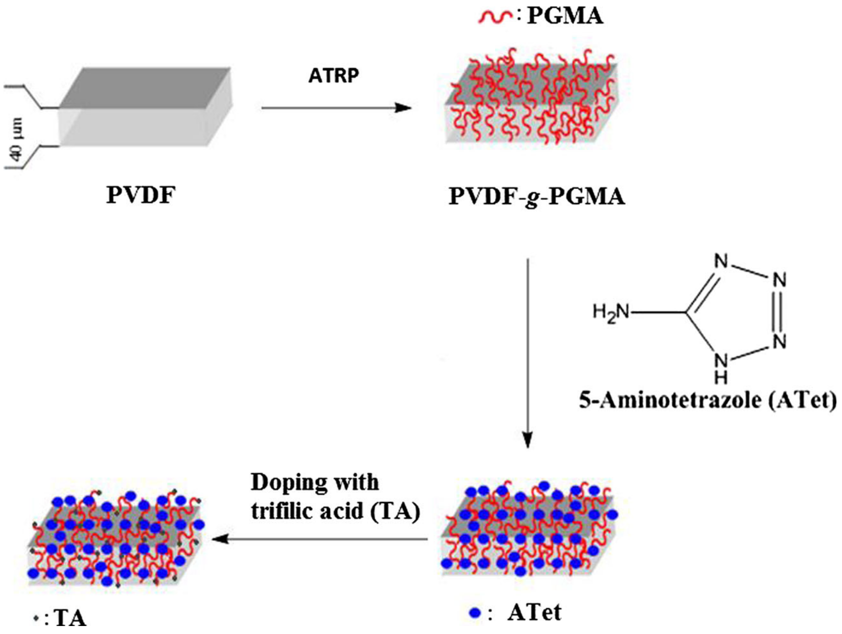

Fig. 2 Synthesis of PVDF-*g*-PGMA-ATet-(TA)x (x=1.0, 2.0, and 4.0) proton conducting membranes by AGET ATRP

Table 1 Tetrazole content of PVDF-*g*-PGMA-ATet calculated by EDS results

Sample	C (%)	F (%)	O (%)	N (%)	Azole (%)*	
PVDF-*g*-PGMA-ATet	38.90	40.36	6.70	9.81	100	Calculated
PVDF-*g*-PGMA-ATet	39.61	44.28	9.10	7.00	71.35	Found

*on a % by weight basis

was poured in water to remove unreacted aminotetrazole and dried under vacuum. A stoichiometric amount of PVDF-*g*-PGMA-ATet films was admixed with TA in DMF at 50 °C for 3 h, and homogeneous solutions of PVDF-*g*-PGMA-ATet-xTA were produced. Solutions with x=1.0, 2.0 and 4.0 moles were prepared,where x is the number of moles of tetrazole per mole of -SO$_3$H. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was evaporated and dried in vacuum oven for several days at 60 °C. The films were stored in glove box for characterizations.

Characterizations

FT-IR spectra were recorded using a Bruker Alpha-P in ATR in the range of 4,000–400 cm^{-1}. ^{1}H-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 N$_2$ 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 bulk composition and the surface morphology of membranes were determined by the energy dispersive X-ray spaectrometry (EDS) method using a scanning electron microscopy (SEM) type JEOL-7001 FESEM (Tokyo, Japan) instrument. All of the samples were previously coated with gold for 150 s in a sputtering device. Carbon, oxygen, flour and nitrogen were measured from three different regions in the samples and the average value is used.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The samples were sandwiched between platinum

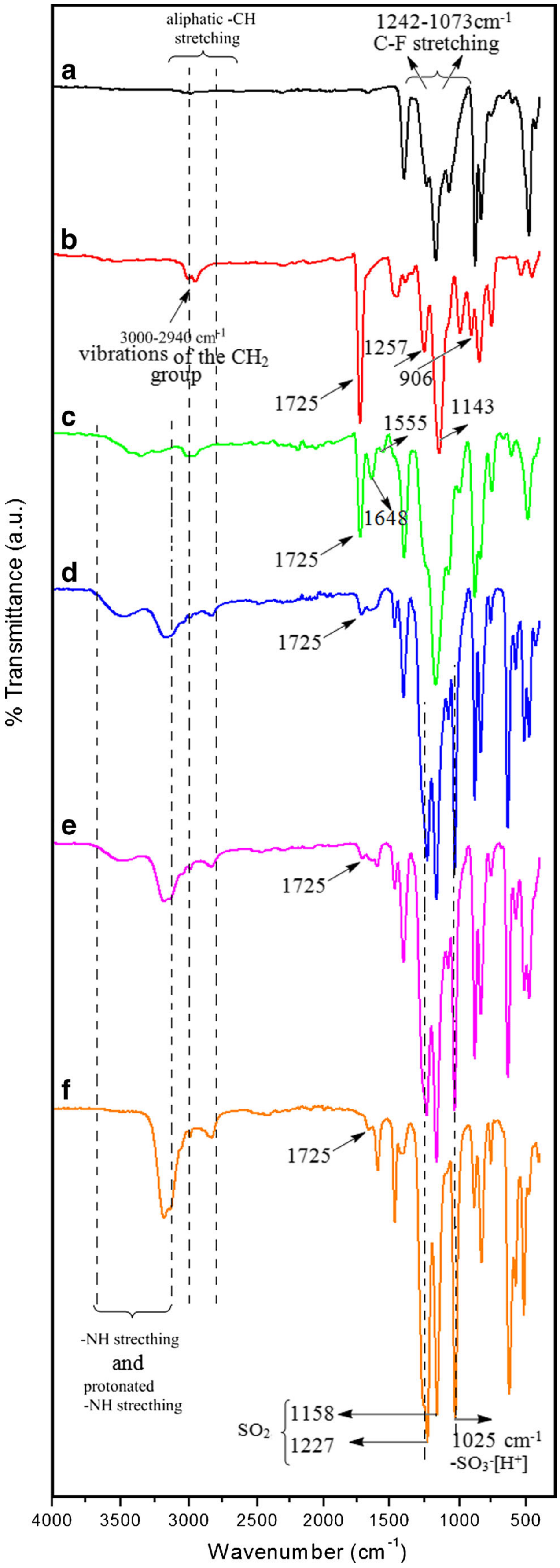

Fig. 3 FTIR spectra of (*a*) PVDF, (*b*) PVDF-*g*-PGMA, (*c*) PVDF-*g*-PGMA-ATet, (*d*) PVDF-*g*-PGMA-ATet-(TA)$_1$, (*e*) PVDF-*g*-PGMA-ATet-(TA)$_2$ and (*f*) PVDF-*g*-PGMA-ATet-(TA)$_4$ ▶

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

Due to the strong binding energy of the C–F bond (486 kJ/mol) [32], initiation efficiency of secondary fluorine in ATRP is supposed to be rather low. Until the report of Mayes and coworkers [32] on the successful ATRP initiated directly by PVDF polymer, it was a common practice to incorporate highly active initiating moieties, such as carbonyl bromine, on the surface of PVDF before conducting ATRP. In the forthcoming works, ATRP initiation by secondary fluorine was also employed in the surface grafting from PVDF films although not much was reported to reveal the initiation step, especially the difficulty in halogen exchange between fluorine and chlorine in the CuCl catalyst,

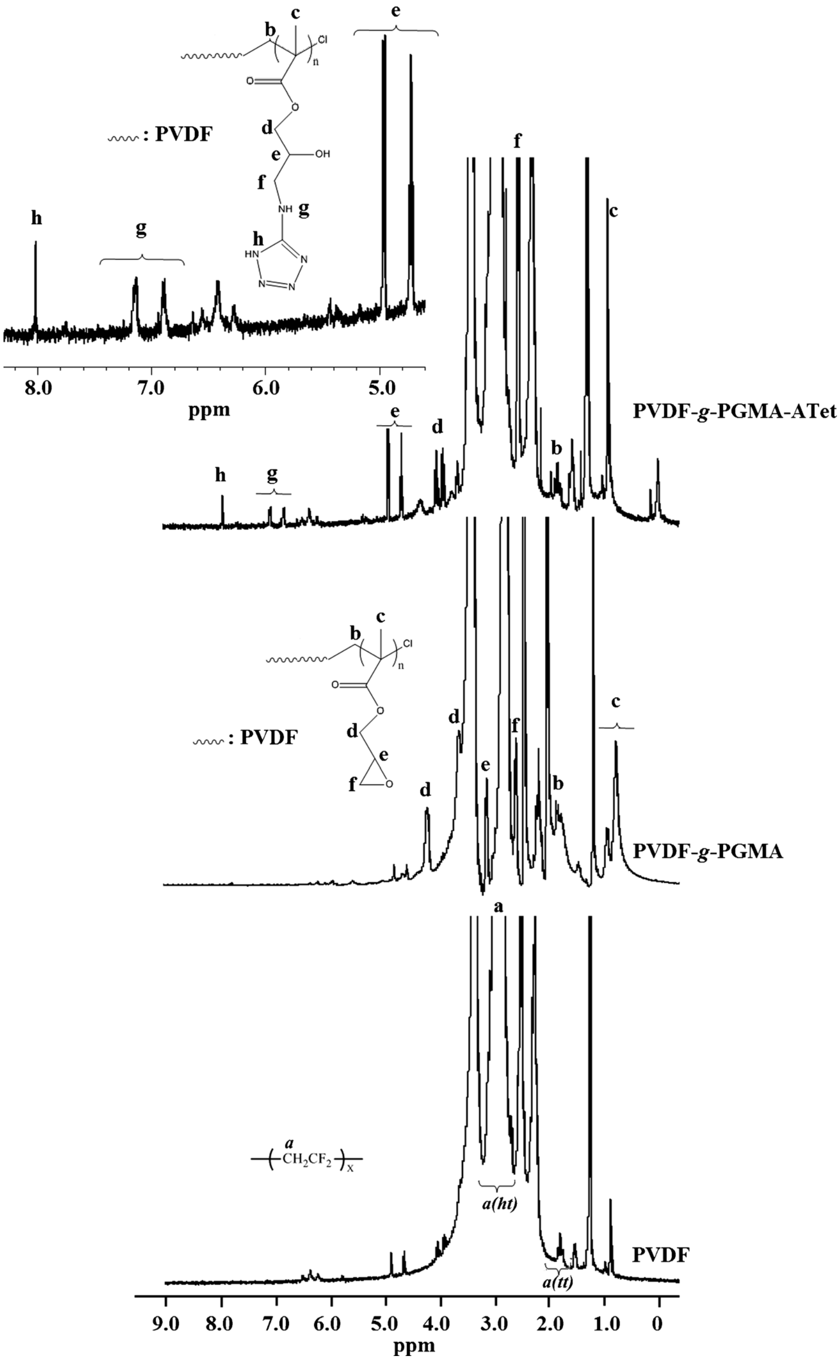

Fig. 4 ^{1}H-NMR spectra of PVDF, PVDF-*g*-PGMA and PVDF-*g*-PGMA-ATet recorded in d^6-DMSO

which stems from stronger C-F binding energy (486 kJ/mol) as compared to that of C-Cl (339 kJ/mol) [30, 33–35, 39]. As expected, relatively low grafting yields were reported in these works. Although the initiation efficiency of fluoride is not high, it provides a simple one-step process for graft ATRP technique.

In the present contribution, PVDF-*g*-PGMA graft copolymers were produced via AGET ATRP of GMA directly from the surface of PVDF at room temperature as illustrated in Fig. 1. Interestingly, the AGET ATRP experiments by using $CuCl_2$, PMDETA, AscA and water did not require high temperatures, which was also consistent with the work of Yuan et al. [39]. Degree of grafting (DG) on the films was determined as about 10 % from the increase in weight after grafting using the following equation:

$$Degree\,of\,Grafting = \frac{Wg - W0}{W0} \times 100$$

where W0 and Wg are the weights of the film before and after grafting, respectively.

Aminotetrazole groups were immobilized via reaction with PVDF-*g*-PGMA by ring opening of the epoxide group as depicted in Fig. 2. The composition of the PVDF based membranes was verified by energy dispersive X-ray spaectrometry (EDS). The results are summarized in Table 1. Aminotetrazole content of the sample, which was calculated on the basis of nitrogen analysis, was determined as 71.35 % by weight. The results confirmed that surface grafting and modification were successful.

Finally, stoichiometric amounts of PVDF-*g*-PGMA-ATet films were admixed with TA in DMF and homogeneous solutions of PVDF-*g*-PGMA-ATet-$(TA)_x$ (x=1.0, 2.0 and 4.0) were produced, where x is the number of moles of TA per mole of aminotetrazole units. Anhydrous PEMs were obtained upon casting of the solutions in polished polytetrafluoroethylene (PTFE) plates and drying.

FT-IR analysis

Infrared spectroscopy was employed to provide information about the chemical structure of the unmodified and modified PVDF membranes. Figure 3 shows the FT-IR spectra of the PVDF base film, PVDF-*g*-PGMA membrane, aminotetrazole functional proton conducting membrane (PVDF-*g*-PGMA-ATet) and triflic acid doped membranes (PVDF-*g*-PGMA-ATet-(TA)x). The asymmetric and symmetric stretching vibrations of the CH_2 group in the PVDF base film (Fig. 3a) were located, respectively, at 3,024 cm^{-1} and 2,982 cm^{-1} [2, 8]. The strong peak which appeared at 1,404 cm^{-1} corresponds to CH_2 stretching vibrations. Strong and wide peaks appearing between 1,242 and 1,073 cm^{-1} correspond to the C-F stretching and were characteristic peaks of the PVDF base film [2, 8]. For the glycidyl methacrylate (GMA) grafted PVDF membranes, PGMA shows the absorption at 903 cm^{-1} which is assigned to strecthing vibration of the epoxy group [14, 40]. Carbonyl group gives a strong peak at 1,725 cm^{-1} and the strong peak at 1,257 cm^{-1} and 1,143 cm^{-1} are attributed to C-O strecthing of the ester group [14]. These signs confirmed that the monomer was grafted onto the PVDF

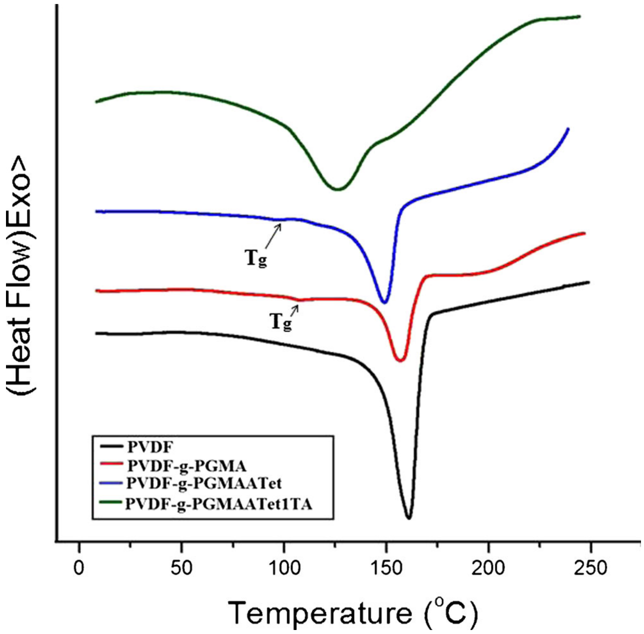

Fig. 5 DSC thermograms of PVDF, PVDF-*g*-PGMA, PVDF-*g*-PGMA-ATet, (d) PVDF-*g*-PGMA-ATet-$(TA)_1$ recorded under N_2 atmosphere at a heating rate of 10 °C/min

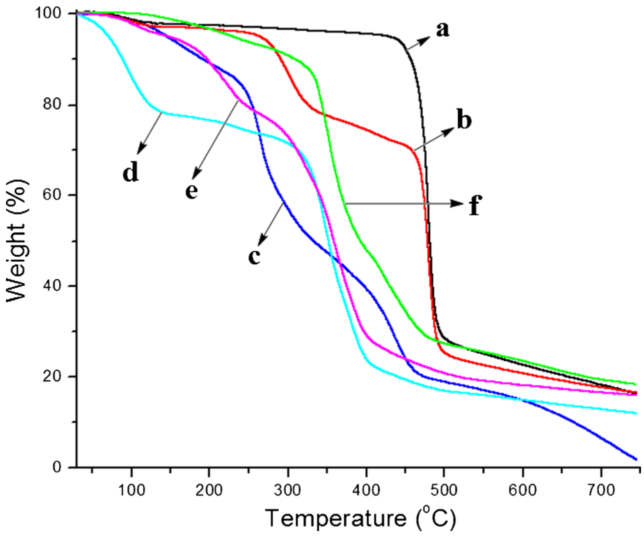

Fig. 6 TG thermograms of (*a*) PVDF, (*b*) PVDF-*g*-PGMA, (*c*) PGMAATet, (*d*) PVDF-*g*-PGMA-ATet-$(TA)_1$, (*e*) PVDF-*g*-PGMA-ATet-$(TA)_2$ and (*f*) PVDF-*g*-PGMA-ATet-$(TA)_4$ polymers at a heating rate of 10 °C/min in inert atmosphere

base films (Fig. 3b). PGMAATet exhibited a medium absorption at 1,648 cm^{-1} and 1,555 cm^{-1} due to amine bond and tetrazole ring vibrations, respectively. The epoxy absorption peak at 906 cm^{-1} disappeared on tetrazole functionalization (Fig. 3c). Figure 3d, e, and f show the FTIR spectra of acid-doped PVDF-PGMA-ATet. Triflic acid gives several absorptions between 1,028 cm^{-1} and 1,227 cm^{-1}. The strong bands at 1,158 and 1,227 cm^{-1} are attributed to SO_2, and a strong absorption peak at 1,025 cm^{-1} most probably belongs to -$SO_3^-[H^+]$. The formation of a peak at around 3,160 cm^{-1} shows the protonation of the triazole rings, in addition to the broad peaks around 3,500 cm^{-1} [2, 8, 16, 41, 42]. These results confirmed that the interaction between polymer and triflic acid occurs both from carbonyl and tetrazole units.

^{1}H-NMR analysis

Figure 4 shows ^{1}H-NMR spectra of PVDF, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-ATet polymers. PVDF-*g*-PGMA graft copolymer was synthesized via AGET-ATRP. For all samples, the peaks of solvent (DMSO) and water appeared at 2.51 and 3.40 ppm, respectively. The ^{1}H-NMR spectrum exhibited the characteristic multiplets centered at 2.9 and 2.3 ppm originating from the methylene groups in $\text{-CH}_2\text{-CF}_2\text{-}\mathbf{CH_2}\text{-CF}_2\text{-CH}_2\text{-CF}_2\text{-}$ and $\text{-CF}_2\text{-}\mathbf{CH_2}\text{-}\mathbf{CH_2}\text{-CF}_2\text{-}$ sequences appearing in the normal tail-to-head and reversed tail-to-tail VDF additions [2, 7, 8, 25, 26]. The methylene groups of PGMA backbone exhibited signals at 1.89 and 1.82 ppm (b). The signals observed at 0.98 and 0.81 ppm (c) are due to the protons in the –CH_3 groups of PGMA. The spectrum also indicated two

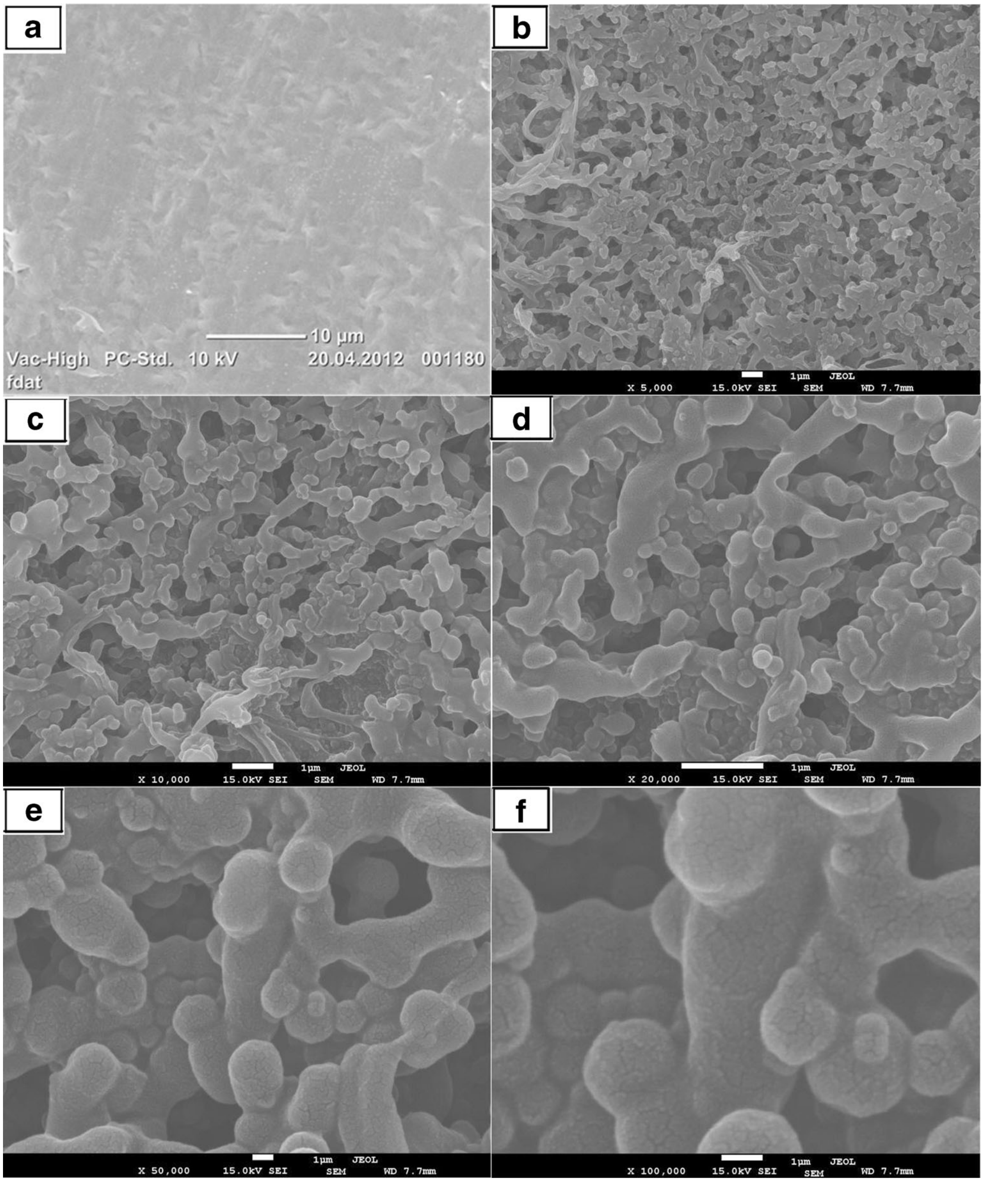

Fig. 7 SEM images of the surface of (**a**) virgin PVDF (10 µm) and PVDF-*g*-PGMA polymer (1 µm) at different magnification, (**b**) 5000×, (**c**) 10000×, (**d**) 20000X, (**e**) 50000×, and (**f**) 100000×, respectively

signals at 4.35 and 3.75 ppm (d), attributable to -$COOCH_2$- group of PGMA. The peaks at 3.2 ppm (e), 2.8 and 2.66 ppm (f) are due to the protons of the oxirane ring [7]. After modification of PVDF-*g*-PGMA with aminotetrazole, the appearance of the peaks belonging to -NH proton of the tetrazole ring at around 8.0 ppm and -CH_2-NH proton of aliphatic chain between 7.10 and 6.90 ppm are a typical indication for the successful achievement of modification reaction as depicted in Fig. 4. The graft copolymerization was evidenced by the ^{1}H-NMR results. Furthermore, ^{1}H-NMR spectra supported the EDS and FTIR results.

Thermal analysis

Thermal stability is an important property of polymer electrolytes during application in PEMFCs. The thermal properties of all samples were investigated with TGA and DSC. Prior to the analysis, the samples were dried under vacuum at 80 °C for 24 h and stored in a glove box. The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. Previously, the glass transition temperature of T_g of the homopolymer (PGMA) was reported as 74 °C [14, 40]. T_g of PVDF was reported at −50 °C [42] and PVDF-*g*-PGMA exhibits a glass transition at approximately 110 °C and melting point (T_m) was observed at approximately 156 °C as depicted in Fig. 5. For the modified PVDF membranes, the T_m was observed due to the presence of ordered PVDF regions. For PVDF-*g*-PGMA-ATet, there is a glass transition temperatures of 98 °C, and melting point (T_m) was measured at approximately 150 °C. The T_g of PVDF-*g*-PGMA-ATet-$(TA)_1$, PVDF-*g*-PGMA-ATet-$(TA)_2$ and PVDF-*g*-PGMA-ATet-$(TA)_4$ are not obvious which may be due to ionic interaction of acid–base units.

The thermal stabilities of base PVDF, PVDF-*g*-PGMA, PGMAATet, and PVDF-*g*-PGMA-ATet(TA)x, (x=1.0, 2.0 and 4.0) proton conducting membranes were studied by TGA as shown in Fig. 6. PVDF showed excellent thermal stability up to 450 °C [2, 8]. The TGA curves of PVDF-*g*-PGMA polymer membranes showed a satisfactory thermal stability up to 275 °C. PVDF-*g*-PGMA polymer decomposes above 275 °C. 20 % of PVDF-*g*-PGMA polymer decomposes at around 325 °C because of degradation of PGMA polymer main chain, after 460 °C, second weight loss region occurs because of degradation of PVDF. The decomposition temperature of tetrazole functional polymer PGMAATet is approximately 230 °C [14]. An elusive weight change until this temperature can be attributed to the loss of absorbed humidity as depicted in Fig. 6(c). After doping the PVDF-*g*-PGMA-ATet functional membranes with triflic acid, the thermal stability of membranes decrease. The highest thermal stability belongs to PVDF-*g*-PGMA-ATet$(TA)_4$ (230 °C) and the other membrane PVDF-*g*-PGMA-ATet$(TA)_2$ is thermally stable up to approximately 200 °C (Fig. 6(d) and (e)). In these acid doped samples, especially PVDF-*g*-PGMA-ATet$(TA)_4$, for the weight loss begins at high temperatures compared with tetrazole functional membrane (PVDF-*g*-PGMA-ATet) as nearly single step. This may be due to the hydrogen bonding between triflic acid and tetrazole units, which hinders the tetrazole unit degradation [14].

Morphology

Surface morphologies of the virgin PVDF membrane and PVDF-*g*-PGMA membranes were investigated by scanning electron microscopy (SEM). In Fig. 7 (a), the PVDF surface is smooth while it has transformed into a hollowed structure in

Fig. 8 AC conductivity versus frequency of PVDF-*g*-PGMA-ATet-$(TA)_4$ at several temperatures

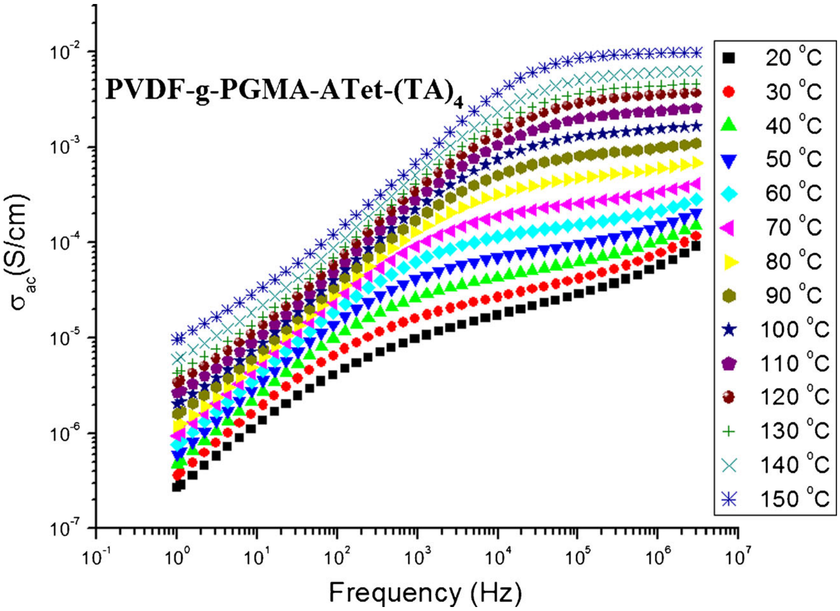

Table 2 Doping ratio with triflic acid, Tg and maximum proton conductivity values of PVDF based membranes

Sample Name	Doping ratio with (TA)	T_g (°C)	Max. Proton Conductivity (Scm^{-1})
PVDF-*g*-PGMA	–	110 °C	–
PVDF-*g*-PGMA-ATet	–	98 °C	–
PVDF-*g*-PGMA-ATet-$(TA)_1$	1:1	**a**	9.04×10^{-5} Scm^{-1} at 150 °C
PVDF-*g*-PGMA-ATet-$(TA)_2$	1:2	**a**	1.3×10^{-3} Scm^{-1} at 150 °C
PVDF-*g*-PGMA-ATet-$(TA)_4$	1:4	**a**	0.011 Scm^{-1} at 150 °C

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

Fig. 7 (b–f) for PVDF-*g*-PGMA, which implies that PGMA was grafted on PVDF surface [43].

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:

$$\sigma^{`}(\omega)=\sigma_{ac}(\omega)=\varepsilon^{``}(\omega)\omega\,\varepsilon_o$$

where $\sigma^{`}(\omega)$ is the real part of conductivity, ω=2πf is the angular frequency, ε_o is the vacuum permittivity ($\varepsilon_o=8.852\times10^{-14}$ F/cm), and $\varepsilon^{``}$is the imaginary part of complex dielectric permittivity (ε^*). The proton conductivities of anhydrous polymer electrolytes were measured from 20 °C to 150 °C. Figure 8 shows the AC conductivity of PVDF-*g*-PGMA-ATet-$(TA)_4$ versus frequency at several temperatures. As expected the proton conductivity increases as temperature increases. In the anhydrous conditions, the proton conductivity of PVDF-*g*-PGMA-ATet-$(TA)_4$ was measured as 0.011 Scm^{-1} at 150 °C (Table 2).

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. The DC curves are closer to linear type curves which can be explained with Arrhenious 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. Arrhenious behavior is generally observed in the matrices where during the

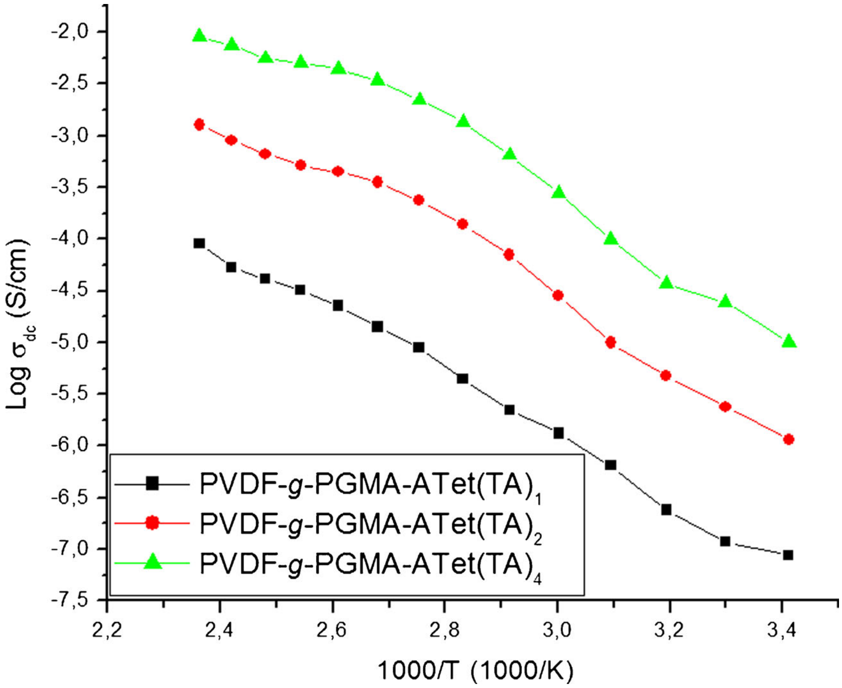

Fig. 9 Variation of the DC proton conductivity of triflic acid (TA) doped PVDF-*g*-PGMA-ATet polymer membranes as a function of reciprocal temperature

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 the grafted matrix, the proton conductivity is carried out between aminotetrazole and triflic acid units. Since the aminotetrazole attachment to PGMA and doping were performed in homogeneous solution, we expect that a matrix with hydrophobic PVDF backbone and a channel with aminotetrazole units might have formed, in which aminotetrazole units interact with triflic acid molecules (Fig. 10).

PVDF has a similar backbone with Nafion and since it is cheaper the scientists tried to mimick the matrix of Nafion by grafting sulfonic acid groups into PVDF via ATRP methods [25–31]. The proton conductivity in these studies were based on the humidity content and consequently these membranes were not suitable for high temperature applications. In our study, proton conduction is based on the tetrazole and triflic acid units and the material can be used at high temperatures. Moreover, PVDF provided a thermally and mechanically stable matrix and good film formability. It can be concluded from the conductivity and FT-IR results that in the highly doped PVDF-*g*-PGMA-ATet, conductivity occurs throughout the material predominantly by Grotthuss mechanism. In the absence of humidity, the proton conductivity of PVDF-*g*-PGMA-ATet-(TA)$_4$ was measured as 0.011 Scm^{-1} at 150 °C. This result also fits with the conductivity reported by Celik et.al. [14]. Possible mechanism of proton transport in

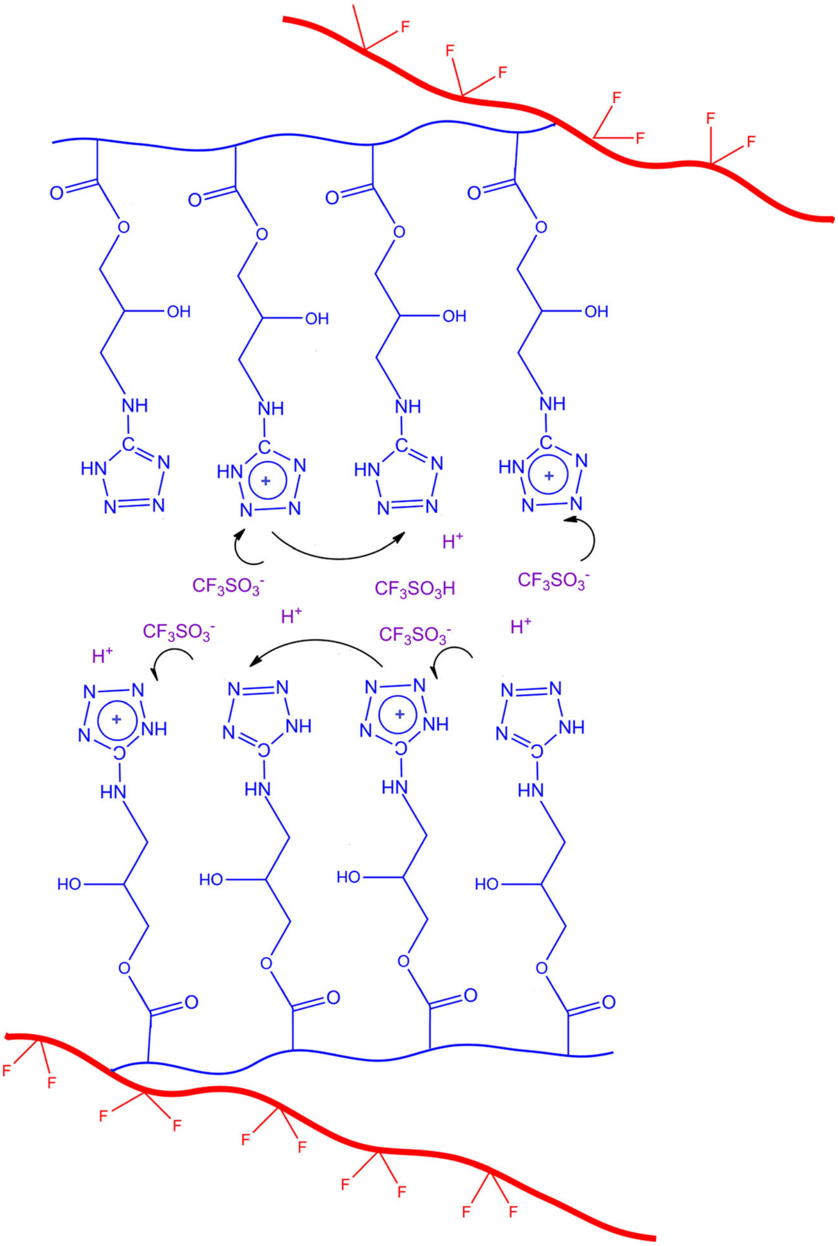

Fig. 10 Possible mechanism of proton transport in PVDF-*g*-PGMA-ATet-(TA)x (*x*=1.0, 2.0 and 4.0) membranes

PVDF-*g*-PGMA-ATet-(TA)x, in which triflic acid is coordinated with aminotetrazole groups is illustrated in Fig. 10.

Conclusions

A PVDF based graft copolymer was prepared via surface initiated AGET-ATRP of GMA at room temperature, followed by a modification reaction with 5-aminotetrazole to achieve PVDF-*g*-PGMA-ATet membrane. Success of grafting was evidenced by FT-IR and ^{1}H-NMR. Modification of the graft copolymer with aminotetrazole was verified by using EDS, FTIR and ^{1}H-NMR. TGA showed that PVDF-*g*-PGMA and PVDF-*g*-PGMA-ATet(TA)$_4$ membranes were thermally stable up to 275 °C and 230 °C, respectively. The proton conductivities were investigated for acid doped membranes. Under anhydrous conditions, PVDF-*g*-PGMA-ATet(TA)$_4$ with a degree of grafting of 10 % showed a maximum proton conductivity of 0.011 Scm^{-1} at 150 °C. The AGET ATRP method used in this work provides a flexible and versatile surface modification method, which shows potential for membrane modification and manufacturing. Therefore, this work would make a contribution to the study of anhydrous polymer electrolyte membranes.

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