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Synthesis of fluorinated polymer electrolyte membranes by radiation grafting and atom transfer radical polymerization techniques

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ABSTRACT

A novel polymer electrolyte membrane was synthesized by radiation-induced grafting and consequent atom transfer radical polymerization (ATRP). First, bromine-containing perfluorinated grafts were prepared by radiation grafting of 2-bromotetrafluoroethyl trifluorovinyl ether (BrTFF) into a poly(ethylene-co-tetrafluoroethylene) (ETFE) film. Then, the bromine atoms in the ETFE-*g*-PBrTFF grafted films were acted as initiators, and the films were treated with Cu(I)-based catalytic system of a CuBr and 2,2′-bipyridyl (bpy) for the ATRP. By adjusting the molar ratio of initiator/CuBr/bpy and the reaction temperature, branched poly(styrene) with a grafting yield of above 100% on the poly(BrTFF) main chains was constructed in ETFE-*g*-PBrTFF films. Thermal analysis revealed that the perfluorinated poly(BrTFF) main chains were miscible to ETFE, whereas the hydrocarbon poly(styrene) branches were phase-separated from the ETFE-*g*-PBrTFF film. Sulfonic groups could be further introduced into the poly(styrene) grafts of ETFE-*g*-PBrTFF-*g*-PS films with homogeneous distribution in a perpendicular direction to the membrane surface. The resulting membrane with a styrene grafting yield of 15% exhibited higher proton conductivity than commercial Nafion 117 membrane. Likewise, it had better chemical stability than ETFE-*g*-PSSA membrane prepared by conventional radiation-induced grafting.

1. Introduction

Polymer electrolyte membrane (PEM) is a vital component of fuel cells, acting as a separator to prevent mixing of the reactant materials while transporting the protons from the anode to the cathodes [1]. Nowadays, Nafion® membrane is the proton-conducting membrane most frequently used in fuel cells because of its excellent chemical stability and high proton conductivity. However, it has obvious shortcomings: high cost, lower stability at higher temperature, poor performance as a gas barrier and high methanol crossover [2]. Therefore, much research has been devoted to develop new PEMs with higher fuel cell performance, for example, non-perfluorinated aromatic membranes [3,4], organic/inorganic hybrid membranes [5], and radiation-induced grafted membranes [6–10].

Radiation-induced grafting is one of the most effective methods for the introduction of active functional groups into the graft polymer chains in the films. In our past work, some PEMs have been developed by the radiation grafting of styrene derivatives such as styrene, vinyltoluene, and divinylbenzene into fluorinated polymer films, followed by sulfonation with chlorosulfonic acid [8–10]. These PEMs have some properties which are markedly superior to Nafion® membranes.

ATRP has been successfully used to prepare well-defined graft polymers [11–13]. For grafting directly onto polymer films by ATRP, commercial halogenated polyolefins, such as poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), and poly(chlorotrifluoroethylene) (PCTFE) are good candidates for the base films because these films contain secondary halogen atoms in their main chains, which are potential ATRP initiators. However, it has been reported that the PVC backbone is inert to ATRP conditions, i.e. ca. 1% of monomer unit of alkyl chloride in PVC was utilized as ATRP initiating sites because even secondary chlorines in the chlorinated films are less reactive for initiating ATRP [14]. On the other hand, well-defined graft polymers also have been synthesized by the

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combination of radiation and ATRP techniques [15]. A halogenated monomer such as vinylbenzyl chloride (VBC) was firstly grafted onto PVDF film, and then the benzyl chloride groups in PVDF-*g*-PVBC film were utilized as initiators for ATRP of styrene into PVDF-*g*-PVBC film. It was found that a higher grafting yield (400%) was reached comparing to that synthesized with conventional radiation-induced grafting method. However, after sulfonation of poly(styrene) graft-chains in PVDF-*g*-PVBC film, the proton conductivity of the resulting PEMs was lower than that of PVDF-*g*-PSSA membrane prepared with radiation alone, which needs to be investigated further for meeting the applications in fuel cells [15].

Recently, we reported the successful grafting of perfluorinated vinyl ether monomer by a simultaneous radiation method [16]. Namely, 2-bromotetrafluoroethyl trifluorovinyl ether (BrTFF), which contains bromine atoms can be grafted into a poly(ethylene-co-tetrafluoroethylene) (ETFE) base film with grafting yield of above 70% (ETFE-*g*-PBrTFF). Taking account of the excellent performance of perfluorinated polymers for the application of the PEMs in fuel cell, we utilized the ETFE-*g*-PBrTFF film as a base polymer for ATRP to obtain the PEMs with high performance. In this work, ATRP of styrene into fluorinated ETFE-*g*-PBrTFF film and the assessing of the resulting PEMs were investigated in detail. It was expected that the resulting new-type fluorinated PEMs would have improved properties for the further application in fuel cells.

2. Experimental

2.1. Materials

The ETFE film (25 μm) was kindly provided by Asahi Glass Co., Japan and was washed with acetone to remove any impurity on its surface before use. 2-Bromotetrafluoroethyl trifluorovinyl ether (BrTFF) was purchased from Matrix Scientific Co. and used without further purification. Styrene, CuBr, 2,2′-bipyridyl (bpy), dimethylformamide (DMF), chlorosulfonic acid, 1,2-dichloroethane, acetone and hexafluorobenzene (HFB) were purchased from Wako Pure Chemical Industries, Ltd., Japan.

2.2. Radiation-induced and ATRP assisted graft polymerization

At first, ETFE-*g*-PBrTFF films (grafting yield = 34.4%) were prepared by radiation-induced grafting of BrTFF into ETFE films at room temperature with the dose of 660 kGy according to the method we reported earlier [16].

Styrene was grafted into the ETFE-*g*-PBrTFF films by the ATRP method. The bromine atom in the films was acted as initiator for the polymerization process. CuBr and bpy were utilized as a catalyst and a ligand for ATRP, respectively. A small amount of DMF (10 vol%) was added to the monomer solution for increasing the solubility of CuBr. The molar ratio of initiator/CuBr/ligand reagent was varied from 0/0/0 to 1/2/4. The reaction temperature and reaction time was varied from 100 to 115 °C and from 1 to 6 h, respectively. Styrene monomer (10 g) was purged with nitrogen for 30 min before grafting, and an inert atmosphere was maintained throughout the reactions. CuBr and bpy dissolved in DMF were mixed with styrene monomer to form homogeneous solution. The solution was heated to the reaction temperature before the ETFE-*g*-PBrTFF film was immersed to commence the ATRP (Scheme 1). After the reaction, the poly(styrene)-grafted films, i.e. ETFE-*g*-PBrTFF-*g*-PS films were Soxhlet-extracted with toluene for 24 h to remove the ungrafted homopolymer and residual monomers. Herein the grafting yield of poly(styrene) into ETFE-*g*-PBrTFF film was expressed as $\mathrm{GY_S}$:

$$\mathrm{GY_S}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \tag{1}$$

where W_1 and W_2 are the weight before and after grafting styrene, respectively.

2.3. Sulfonation of the grafted films and evaluation of the resulting PEMs

The ETFE-*g*-PBrTFF-*g*-PS films were sulfonated in a 0.2 mol $\mathrm{L^{-1}}$ chlorosulfonic acid solution of 1,2-dichloroethane at 50 °C for 6 h, and then hydrolyzed with distilled water at 60 °C for 12 h.

The ion exchange capacity (IEC) of the resulting ETFE-*g*-PBrTFF-*g*-PSSA PEM was determined by acid–base titration. The dried membrane in the protonic form was immersed in 20 mL of 3 mol $\mathrm{L^{-1}}$ NaCl aqueous solution and equilibrated for 24 h. The solution was then titrated with NaOH solution using an automatic titrator (HIRANUMA COM-555) until pH 7.0 was reached. Based on the titration results, the IEC (mmol $\mathrm{g^{-1}}$) was calculated as follows:

$$\mathrm{IEC} = \frac{cV_{\mathrm{NaOH}}}{W_{\mathrm{d}}} \tag{2}$$

where c (mol $\mathrm{L^{-1}}$) is the concentration of NaOH solution, V_{NaOH} (mL) is the volume of the NaOH solution consumed in the titration, and W_{d} (g) is the dry weight of the PEM in the protonic form.

The proton conductivity of the PEM was measured by impedance spectroscopy using a Solartron 1269 analyzer with an ac perturbation of 10 mV. The samples were immersed in 20 mL 1 mol $\mathrm{L^{-1}}$ HCl to the protonic form for 8 h, then hydrated in water at 25 °C for 12 h before the measurement. The samples were clamped between two Pt electrodes of the apparatus, and the impedance spectroscopy was measured after wiping off the excess water on the membrane surface. The conductivity (σ, S $\mathrm{cm^{-1}}$) was calculated from the impedance data using the following relation:

$$\sigma = \frac{d}{Rtl} \tag{3}$$

where d (cm) is the distance of the two electrodes, t (cm) is the membrane thickness and l (cm) is the length of the membrane along the electrode. R (Ω) was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the real axis.

The water uptake of the PEM was determined as follows. First, the membrane was immersed in deionized water at 25 °C for 24 h; then the membrane was taken out of the water and weighed after wiping off the excess surface water. The water uptake was estimated using the following equation:

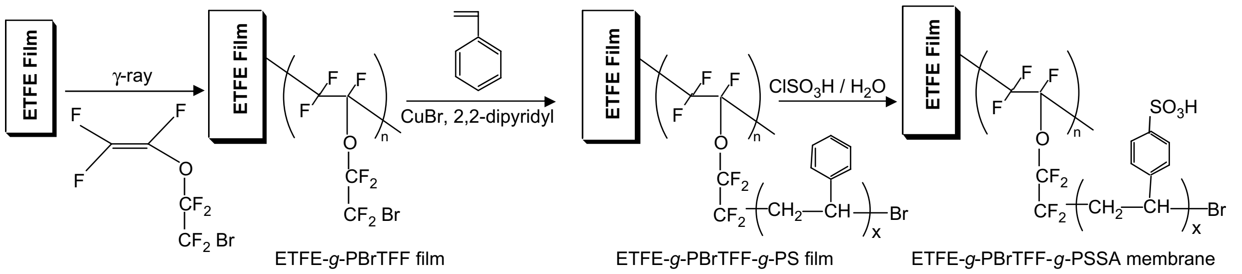
$$\text{Water uptake}(\%) = \frac{W_{\mathrm{w}} - W_{\mathrm{d}}}{W_{\mathrm{d}}} \times 100 \tag{4}$$

where W_{w} and W_{d} are the weights of the membrane in the wet and dry states, respectively.

2.4. Structure analyses of the grafted films and the resulting PEMs

The Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of the films were recorded with a FT-IR 710 (Horiba, Japan) equipped with a diamond ATR cell.

The thermal properties were characterized by the thermogravimetric analysis (TGA) of the films using a Thermo Plus2/TG-DTA (Rigaku, Japan). The specimen of ca. 5 mg was heated to 550 °C at a heating rate of 10 °C $\mathrm{min^{-1}}$ with the nitrogen flow rate of 100 mL $\mathrm{min^{-1}}$.



Scheme 1. Synthesis route of ETFE-*g*-PBrTFF-*g*-PSSA membrane.

The depth profiles of sulfur atoms of the sulfonic acid groups and bromine atoms of poly(BrTFF) in the perpendicular direction of the PEM was measured by a JEOL JSM-5600 scanning electron microscope (SEM) connected with an energy dispersive X-ray spectroscopy (EDS) and operated at a voltage of 15 kV. The cross-section of the sample was prepared by cutting the membrane with a knife after immersion in liquid nitrogen, and subsequent coating with carbon.

2.5. Chemical stability

The chemical stability of the PEM was evaluated in a 3% H_2O_2 aqueous solution at 60 °C. During the immersion, the membrane was intermittently taken out of the solution and weighed after wiping off the excess surface water. The index of chemical stability is the durability time, which is defined as the time when the weight of the membrane decreases to less than the initial weight.

3. Results and discussion

3.1. Synthesis of ETFE-g-PBrTFF-g-PSSA membranes

It was reported that a Cu(I)-based catalytic system of CuBr and bpy is effective for the ATRP of styrene [15,17]. In this work, we investigated the ATRP of styrene into ETFE-g-PBrTFF film with this Cu(I)-based catalytic system to develop fuel cell electrolyte membranes containing the PSSA branched-fluorinated grafts which are proton-conducting phase. Fig. 1 shows the influence of the molar ratio of initiator/CuBr/bpy on the ATRP of styrene into ETFE-*g*-PBrTFF film at 110 °C. The grafting of styrene in the absence of bromide initiators almost did not proceed from an ETFE film whether with or without ATRP reagents (initiator/CuBr/bpy = 0/0/0 or 0/1/2). In contrast, the grafting of styrene proceeded well from ETFE-*g*-PBrTFF, which has bromine atoms as initiators, with ATRP reagents, achieving a poly(styrene)-grafted ETFE-*g*-PBrTFF film (ETFE-*g*-PBrTFF-*g*-PS film). When the molar amount of bpy was present in two or three times excess of the initiator and CuBr, (initiator/CuBr/bpy = 1/1/2 or 1/1/3), a higher grafting yield of poly(styrene) (GYs), ca. 46%, was obtained. In the ATRP of styrene onto PVDF-*g*-PVBC film, it has been observed when the molar amount of bpy was present in three times excess of the initiator and CuBr, there was the fastest grafting polymerization of styrene [15]. Styrene also can be grafted into ETFE-*g*-PBrTFF without adding ATRP reagents (initiator/CuBr/bpy = 1/0/0) though with lower GY_S (16.8%) than those with the ATRP reagents. Due to the relatively higher grafting temperature of 110 °C, thermal polymerization has occurred [18]; however, this thermally induced grafting must have occurred at the surface of the ETFE-*g*-PBrTFF films because we observed that only the thickness of the grafted film was increased and its color changed to white after grafting. These results suggest that the bromine groups in ETFE-*g*-PBrTFF film act effectively as initiators with ATRP reagents to cause the grafting reaction of styrene.

The effect of reaction time and temperature on the ATRP of styrene into ETFE-*g*-PBrTFF film is shown in Fig. 2. The GY_S increased linearly with the reaction time, reaching 120% without leveling off at least under the grafting conditions tested here. The GY_S also increased almost linearly with reaction temperature; the rate of grafting reaction was strongly temperature-dependent within the experimental temperature range of 100–115 °C. The activation energy was calculated with Arrhenius equation below (equation (5)) to be 209 kJ mol^{-1}, which is similar to that of the ATRP of styrene into PVDF-*g*-PVBC film (217 kJ mol^{-1}) in a homogeneous system [16].

$$\ln k_g = \ln A - E_a/RT \qquad (5)$$

where k_g is the rate constant of the grafting reaction (%h^{-1}), A is a constant, E_a is the activation energy of the grafting reaction (kJ mol^{-1}), R is the universal gas constant (8.314 × 10^{-3} kJ mol^{-1} K^{-1}), and T is the reaction temperature (K).

The poly(styrene) branches of ETFE-*g*-PBrTFF film were sulfonated in a chlorosulfonic acid solution and then hydrolyzed in hot water to obtain the PEM, i.e. ETFE-*g*-PBrTFF-*g*-PSSA membrane. The introduction of sulfonic acid ($-SO_3^-$) groups into the grafted film created hydrophilic phase. PEM's good ion exchange capacity, proton conductivity and water uptake are all ascribed to the formation of this hydrophilic phase in the membrane.

3.2. Structural analysis of the grafted films and the resulting PEMs

Fig. 3 shows the FTIR spectra of the original ETFE, ETFE-*g*-PBrTFF, ETFE-*g*-PBrTFF-*g*-PS and ETFE-*g*-PBrTFF-*g*-PSSA films in the range

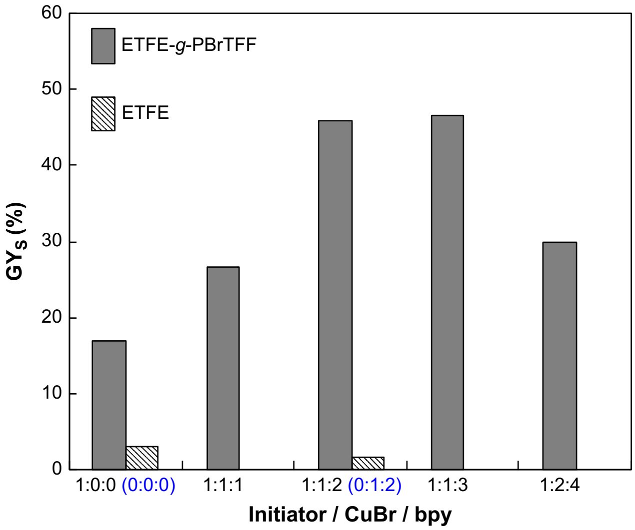


Fig. 1. ATRP of styrene into ETFE-g-PBrTFF film at different molar ratio of initiator/CuBr/bpy. Reaction temperature: 110 °C; reaction time: 3 h.

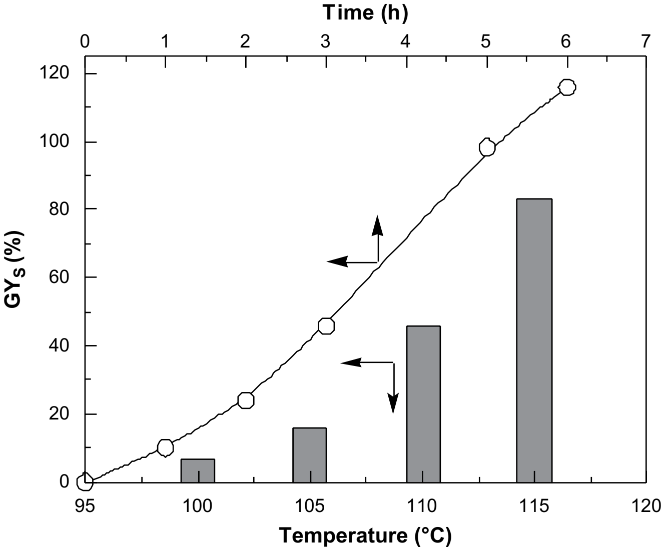


Fig. 2. ATRP of styrene into ETFE-*g*-PBrTFF film at different temperature (3h) and time (110 °C). Initiator/CuBr/bpy = 1/1/2.

630–3800 cm^{-1}. The grafting yields of poly(BrTFF) grafts in the ETFE-*g*-PBrTFF film and poly(styrene) branches in the ETFE-*g*-PBrTFF-*g*-PS were 34.4% and 16.8%, respectively. In the original ETFE film, the sharp absorption band at 1454 cm^{-1} represented the CH deformation, whereas the strong absorption bands in the range of 1000–1300 cm^{-1} were assigned to the absorption of CF_2 groups [19]. The poly(BrTFF) grafted film, ETFE-*g*-PBrTFF, showed a new absorption at 933 cm^{-1}, which was assigned to the OC_2F_4Br group in the grafts as compared to the OC_3F_7 group of trifluorovinyl heptafluoropropyl ether ($CF_2{=}CF{-}O{-}C_3F_7$) [16,20]. When the ETFE-*g*-PBrTFF film was further grafted with styrene by the ATRP, obvious absorption of poly(styrene) at 699 cm^{-1} (C–C wagging band) appeared in the spectrum of the ETFE-*g*-PBrTFF-*g*-PS film [21]. The sulfonation of the poly(styrene) branches was confirmed by the presence of the sharp absorption bands at 833 cm^{-1} and 1005 cm^{-1}, which were assigned to the absorption of the $-SO_3^-$ groups in the ETFE-*g*-PBrTFF-*g*-PSSA membrane. Moreover, the absorption bands of a mono-substituted aromatic ring at 699 cm^{-1} disappeared, indicating that the benzene ring in poly(styrene) had been completely sulfonated.

Fig. 4 shows the TG curves of the original ETFE, ETFE-*g*-PBrTFF, ETFE-*g*-PBrTFF-*g*-PS and ETFE-*g*-PBrTFF-*g*-PSSA films in the temperature range of 25–550 °C. The grafting yields of poly(BrTFF) grafts in the ETFE-*g*-PBrTFF film and poly(styrene) branches in the ETFE-*g*-PBrTFF-*g*-PS were 34.4% and 29.8%, respectively. The decomposition temperature obtained from the TG curve was defined as the point where the weight loss was 5%. As shown in Fig. 4, the decomposition temperature of the original ETFE film was 460 °C. ETFE-*g*-PBrTFF film had a lower decomposition temperature, 370 °C, due to radiation-induced cross-linking and double bond formation in ETFE matrix during the period of high-dose radiation grafting (660 kGy) [16]. This degradation seems to occur in one step, indicating that the perfluorinated poly(BrTFF) grafts and a partially fluorinated ETFE film are miscible to each other. Contrary to the poly(BrTFF) grafts, ETFE-*g*-PBrTFF-*g*-PS film exhibited an obvious two-step degradation pattern with an onset decomposition temperature of 345 °C. This is because poly(styrene) branches, consisting of hydrocarbons, and ETFE-*g*-PBrTFF film, consisting of fluorine rich grafts and the original film, are immiscible; thus, these two phases degrade at different decomposition temperatures [22].

There were four weight loss steps along the TG curves for the ETFE-*g*-PBrTFF-*g*-PSSA films. The first weight loss appeared in the temperature range from 80 to 150 °C, which likely was the evaporation of bound water in the membrane. On the basis of the results of the TG/FTIR investigations of radiation-grafted membranes by Gupta et al. [23], the isolated three weight loss stages at 240–310, 310–420 and above 460 °C were considered to be the desulfonation, dearomatization and finally the degradation of the ETFE-*g*-PBrTFF backbone, respectively. The presence of these three isolated decomposition processes indicated that the resulting PEM had considerable heterogeneity [24]. Furthermore, it was found that the ETFE-*g*-PBrTFF, ETFE-*g*-PBrTFF-*g*-PS and ETFE-*g*-PBrTFF-*g*-PSSA films yielded ca. 8%, 13% and 30% residual char at the final heating temperature of 550 °C, respectively. However, in our past work, it

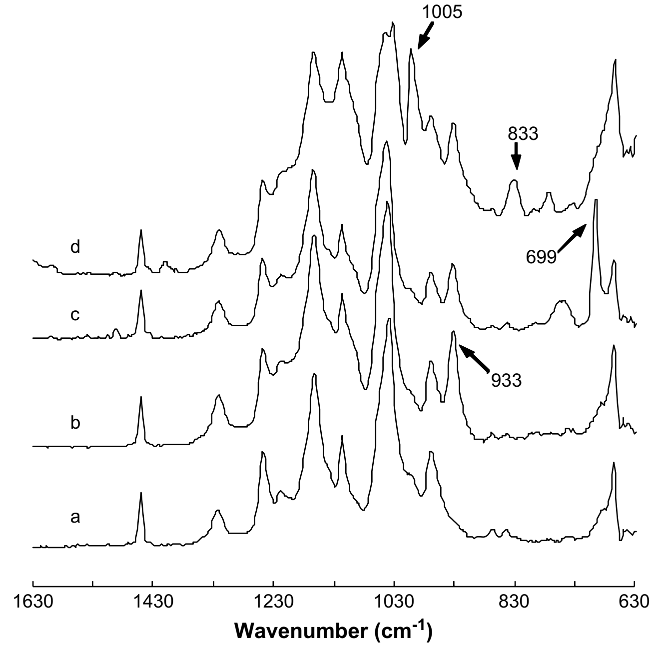


Fig. 3. FTIR spectra of the original ETFE film (*a*), ETFE-*g*-PBrTFF film (*b*), ETFE-*g*-PBrTFF-*g*-PS film (*c*, GY$_S$ = 16.8%), ETFE-*g*-PBrTFF-*g*-PSSA membrane (*d*, GY$_S$ = 16.8%).

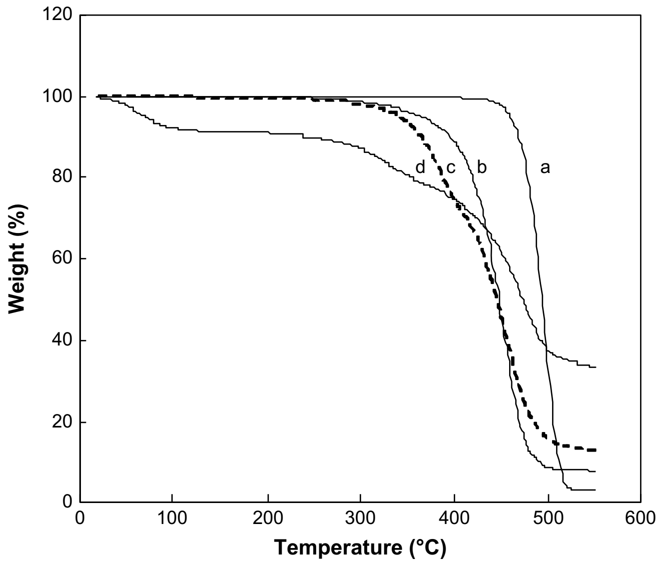


Fig. 4. TG thermograms of the original ETFE film (*a*), ETFE-*g*-PBrTFF film (*b*), ETFE-*g*-PBrTFF-*g*-PS film (*c*, GY$_S$ = 29.8%), ETFE-*g*-PBrTFF-*g*-PSSA membrane (*d*, GY$_S$ = 29.8%).

was found that the films of ETFE grafted with styrene derivatives can decompose completely [9]. These results indicated that the presence of bromine atoms and sulfonic acid groups in the membranes induced carbonization during their thermal decomposition.

The distribution of $-SO_3^-$ groups in the perpendicular direction of the PEM was characterized by SEM-EDS. Fig. 5 shows the EDS of bromine and sulfur in the transverse plane of ETFE-*g*-PBrTFF-*g*-PSSA membrane. It is obvious that there was homogeneous distribution of bromine and sulfur atoms in the perpendicular direction even with quite low GY_S (16.8%), indicating homogeneous distribution of $-SO_3^-$ groups in the ETFE-*g*-PBrTFF-*g*-PSSA membrane. Homogeneous distribution of $-SO_3^-$ groups in a perpendicular direction to the membrane surface is favorable for application of these membranes in fuel cells. In addition, the EDS of bromine in the resulting PEM also showed that the bromine atoms in ETFE-*g*-PBrTFF film successfully initiated the grafting of styrene by the ATRP.

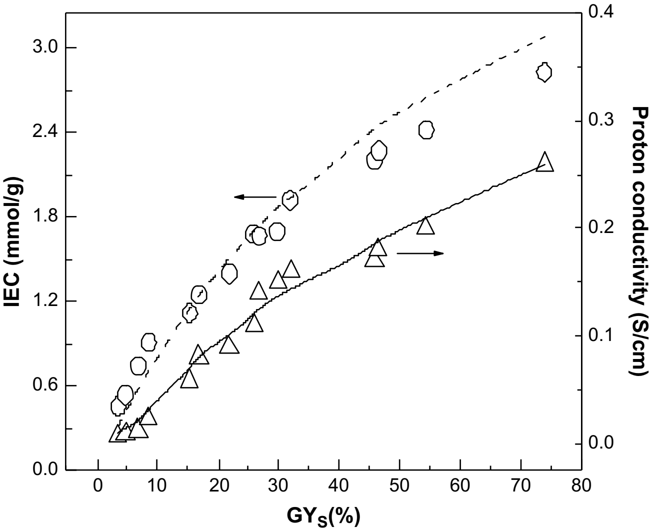


Fig. 6. Ion exchange capacity and proton conductivity of ETFE-*g*-PBrTFF-*g*-PSSA membrane.

3.3. IEC, proton conductivity and water uptake

IEC is an important property affecting the membrane conductivity. Effect of GY_S on the IEC of ETFE-*g*-PBrTFF-*g*-PSSA membranes is shown in Fig. 6. The membrane exhibited high IEC as expected, and the IEC increased with the GY_S, similar to ETFE-*g*-PSSA membranes [25]. The theoretical IEC of the membranes ($IEC_{theor.}$) was calculated according to equation (6) [26,27] and is shown in Fig. 6.

$$IEC_{theor.} = 1000 \times GY_S/(100 \times M_{St} + GY_S \times M_{SSA}) \tag{6}$$

where M_{St} is the molecular weight of styrene (104 g mol^{-1}) and M_{SSA} is the molecular weight of styrene sulfonic acid (SSA, 184 g mol^{-1}). In Fig. 6 it can be seen that the measured IEC increased with increase in GY_S and is close to $IEC_{theor.}$ where GY_S is below 30%; while at higher GY_S, the measured IEC was somewhat lower than $IEC_{theor.}$. This maybe attributed to incompletable sulfonation of poly(styrene) branches inside the membrane. Similar results also were observed in our previous experiment of sulfonation of poly(styrene) grafted in fluoropolymer films [27,28]. The IEC of Nafion 117 has been reported to be 0.97 mmol g^{-1} [10]. Hence, when the GY_S is more than 10%, ETFE-*g*-PBrTFF-*g*-PSSA membranes exhibit higher IEC than Nafion 117.

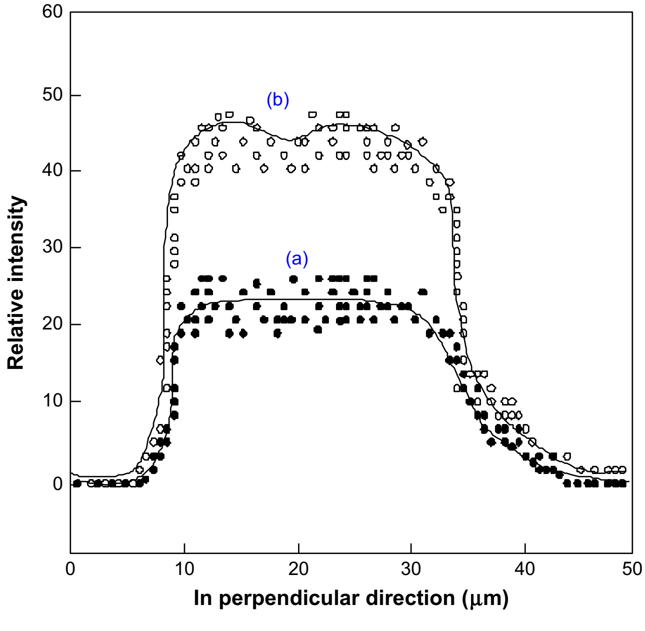


Fig. 5. EDS of bromine (a) and sulfur (b) in the perpendicular direction of ETFE-*g*-PBrTFF-*g*-PSSA membrane (GY_S = 16.8%).

The proton conductivity depends on the number of available acid groups (IEC) and their dissociation capability in water. Effect of GY_S on the proton conductivity of ETFE-*g*-PBrTFF-*g*-PSSA membranes is also shown in Fig. 6. It was found when the GY_S was at low value, such as 3.5%, the membrane already exhibited conductivity (0.007 S cm^{-1}); and when the GY_S was more than 15%, the membrane exhibited higher proton conductivity than that of Nafion 117 (0.06 S cm^{-1}). Compared with ETFE-*g*-PSSA membrane prepared by conventional radiation-induced grafting, the conductivity of the ETFE-*g*-PBrTFF-*g*-PSSA membrane was slightly higher at the same IEC [25], and far exceeded that of the PVDF-TEMPO graft-PSSA membranes (0.01–0.08 S cm^{-1}) [29] and PVDF-*g*-PVBC-*g*-PSSA membranes (0.017–0.07 S cm^{-1}) [15]. Holmberg et al. [29] prepared PVDF-TEMPO graft-PSSA membranes by the combination of radiation chemistry of polymers with nitroxide-mediated living free radical (2,2,6,6-tetramethylpiperidinyl-1-oxy, TEMPO) grafting polymerization with subsequent sulfonation. But in this system, the grafting yield is lower than 20%, lower proton conductivity attribute to lower grafting yield. Holmberg et al. [15] also prepared PVDF-*g*-PVBC-*g*-PSSA membranes by ATRP of styrene onto PVDF-*g*-PVBC membrane. Although the resulting PVDF-*g*-PVBC-*g*-PSSA membrane has high grafted yield, the proton conductivity is relatively low due to the non-fluorinated molecular structure of poly (VBC) grafts in PVDF-*g*-PVBC-*g*-PSSA membrane. However, in our system, the ETFE-*g*-PBrTFF-based film has perfluorinated molecular structure, which is hydrophobic, PSSA branch-chain grafted ETFE-*g*-PBrTFF film is hydrophilic, thus ETFE-*g*-PBrTFF-*g*-PSSA membrane has good proton conductivity. The refined hydrophilic PSSA branch-chain and hydrophobic poly(BrTFF) graft-chain structure in the ETFE-*g*-PBrTFF-*g*-PSSA membrane may form a peculiar hydrophilic–hydrophobic region where the protons can be easily transported.

The water uptake is an important parameter of the PEM which is related to the conductivity and dimensional stability of the membrane. Fig. 7 shows the effect of GY_S on the water uptake and hydration number (n) of the ETFE-*g*-PBrTFF-*g*-PSSA membrane. Here, the hydration number (n), i.e. the number of water molecules per sulfonic acid group in the PEM, was calculated according to

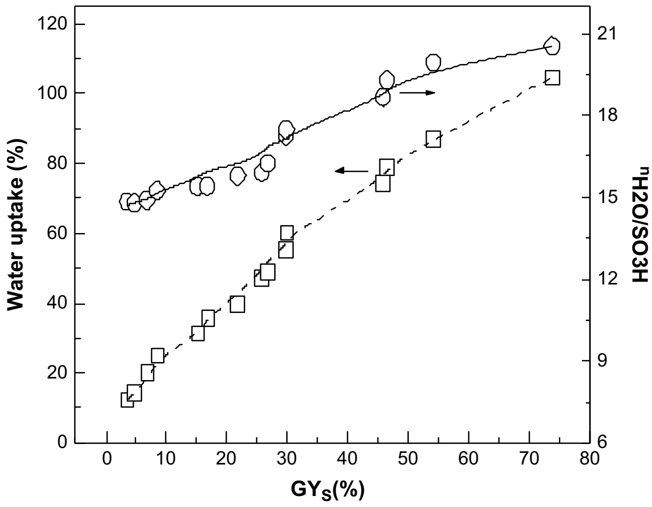


Fig. 7. Water uptake and hydration number of ETFE-*g*-PBrTFF-*g*-PSSA membrane.

equation (7). The water uptake and hydration number gradually increased with increase of GY_S. The water uptake and hydration number of Nafion 117 membrane was reported to be ca. 26% and 17, respectively [1,7], which are similar to those of the ETFE-*g*-PBrTFF-*g*-PSSA membrane with an IEC of 0.97 $\mathrm{mmol\,g^{-1}}$ (ca. 25% and 15).

$$n = \frac{\text{water uptake}}{1.8 \times \text{IEC}} \tag{7}$$

3.3.1. *Chemical stability*

During the fuel cell operation, the H_2O_2 is generated by oxygen diffusion through the membrane and incomplete reduction at the fuel cell anode, bringing about severe degradation of the membrane. Testing the lifetimes of the PEM in an actual fuel cell is both time-consuming and expensive. Thus, it is desirable to develop rapid and simple methods for evaluating the new candidate membranes. In this study, the chemical stabilities of the ETFE-*g*-PBrTFF-*g*-PSSA and ETFE-*g*-PSSA (prepared by radiation-induced grafting as a control) electrolyte membranes were tested in a 3% H_2O_2 aqueous solution at 60 °C. As shown in Fig. 8, the membranes continuously swelled and then decomposed. The durability times of the ETFE-*g*-PBrTFF-*g*-PSSA and ETFE-*g*-PSSA membranes were 20 h and 7 h, respectively. Thus, the ETFE-*g*-PBrTFF-*g*-PSSA membrane was more stable than the ETFE-*g*-PSSA membrane with the same content of poly(SSA) chains, it was thought that poly(BrTFF) grafts inhibited the scission of poly(SSA) branches from the ETFE-*g*-PBrTFF-*g*-PSSA membrane.

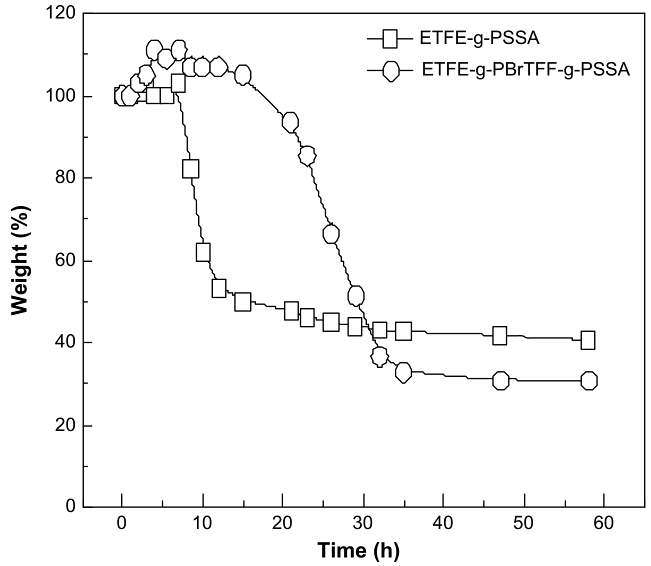


Fig. 8. Chemical stability of ETFE-*g*-PBrTFF-*g*-PSSA membrane ($GY_S = 45.8\%$) and ETFE-*g*-PSSA membrane ($GY_S = 45.0\%$) in 3% H_2O_2 solution at 60 °C.

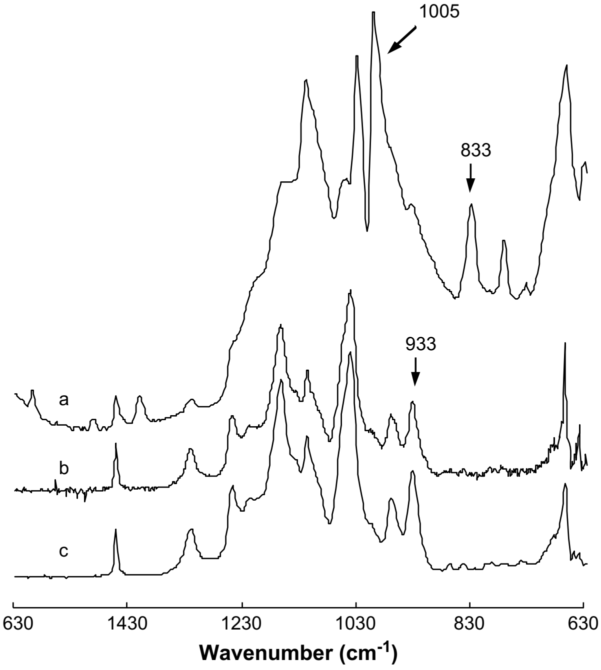


Fig. 9. The change of FTIR spectra of ETFE-*g*-PBrTFF-*g*-PSSA membrane ($GY_S = 45.8\%$) before (a) and after (b) decomposition in 3% H_2O_2 solution at 60 °C. (c) FTIR spectrum of ETFE-*g*-PBrTFF film as a control.

The decomposed membrane was further analyzed with FTIR, and the results are shown in Fig. 9. After decomposition, the absorption bands of the $-SO_3^-$ group in ETFE-*g*-PBrTFF-*g*-PSSA membrane at 833 cm^{-1}, 1005 cm^{-1} disappeared, indicating that poly(SSA) chains were cut and eluted out from the ETFE-*g*-PBrTFF-*g*-PSSA membrane due to the low stability of aromatic sulfonic acid and the presence of a benzyl proton in the poly(styrene) branches [30]. It was also found that decomposed ETFE-*g*-PBrTFF-*g*-PSSA membrane (Fig. 9b) had a FTIR spectrum similar to that of ETFE-*g*-PBrTFF film (Fig. 9c), suggesting that the ETFE-*g*-PBrTFF matrix has excellent chemical stability with its fluorinated molecular structure. In further experiments, we wish to utilize the bromine atoms of ETFE-*g*-PBrTFF film for direct sulfonation or for initiating the ATRP of other monomers and cross-linker for excellent chemical stability.

4. Conclusions

ETFE-*g*-PBrTFF films were prepared firstly by radiation-induced grafting of BrTFF into ETFE films, and then with the aid of a Cu(I)-based catalytic system of CuBr and bpy, poly(styrene) was grafted into the ETFE-*g*-PBrTFF films by using their bromine atoms as initiators for ATRP, thus successfully forming new-type PEMs of ETFE-*g*-PBrTFF-*g*-PSSA. When the molar ratio of initiator/CuBr/bpy was 1/1/2 or 1/1/3, a high grafting yield of poly(styrene) was obtained. The reaction rate was strongly temperature-dependent within the experimental temperature range of 100–115 °C, and the activation energy was calculated to be 209 $\mathrm{kJ\,mol^{-1}}$ with an

Arrhenius equation. Structural analysis of the grafted films and the resulting PEMs indicated that the perfluorinated poly(BrTFF) main chain is miscible to ETFE, whereas the hydrocarbon poly(styrene) branches are phase-separated from the ETFE-*g*-PBrTFF film, and there is homogeneous distribution of sulfonic groups in a perpendicular direction to the membrane surface of the PEM. Further evaluation of the PEM's effectiveness in a fuel cell showed that the PEM with above 15% GY_S exhibited higher proton conductivity than that of commercial Nafion membranes. Furthermore, it had better chemical stability than an ETFE-*g*-PSSA membrane prepared with a conventional radiation technique. We hope that this work provides new ideas for the design of the PEM of fuel cells.

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