Polymer Electrolyte Membranes Having Sulfoalkyl Grafts into ETFE Film Prepared by Radiation-Induced Copolymerization of Methyl Acrylate and Methyl Methacrylate

Truong Thi Hanh,[1,2] Shuichi Takahashi,[1] Jinhua Chen,[1] Shin-ichi Sawada,[1] Yasunari Maekawa[1]

[1]*Conducting Polymer Materials Group, Quantum Beam Science Directorate, Japan Atomic Energy Agency (JAEA), 1233 Watanuki, Gunma 370-1292, Takasaki, Japan*
[2]*Research and Development Center for Radiation Technology, Vietnam Atomic Energy Commission (VAEC), 59 Ly Thuong Kiet, Hanoi, Vietnam*

ABSTRACT: Polymer electrolyte membranes (PEMs) containing alkylsulfonic acid grafts can be prepared by radiation-induced graft copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) into a poly(ethylene-*co*-tetrafluoroethylene) film followed by sulfonation of the MA units in the copolymer grafts using an equimolar complex of chlorosulfonic acid and 1,4-dioxane ($ClSO_3H$-Complex). PEMs with MA/MMA copolymer grafts that are 33%–79% MA units were prepared by preirradiation with a dose of 20 kGy and grafting in bulk comonomers at 60°C. The grafted films are treated with $ClSO3H$-Complex to obtain PEMs with ion exchange capacity of 0.36-0.81 mmol/g (sulfonation degrees of 20%–40%) and proton conductivity of 0.04-0.065 S/cm. These values can be controlled by changing the MA content the sulfonation occurring at an α-carbonyl carbon. The PEMs with higher MMA content showed higher durability in water (80°C) and under oxidative conditions (3% H_2O_2) at 60°C. This is because the PMMA grafts in the PEMs have no proton at an α-carbonyl carbon, which is considered to be a trigger of the degradation of grafting polymers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 231–237, 2009

Key words: polymer electrolyte membranes; radiation grafting; graft copolymerization; alkylsulfonic acid; durability

INTRODUCTION

During the past few years, the direct conversion of chemical energy into electrical energy via fuel cells has been at the center of attention in electrochemical research and technology development. This is due not only to the scientific attraction of fuel cell reactions and the general awareness of the technological potential of fuel cells, but also to society's demand to develop environmentally friendly power generation. Among the various fuel cell types, polymer electrolyte membrane (PEM) fuel cells are of particular interest as power sources in transport, stationary, and portable applications, because they use a flexible and a cheap polymer membrane for the solid electrolytes involved in the proton transport and electrode separation, and operate at relatively low temperatures (<150°C). Commercial perfluorinated ionomer membranes such as Nafion®, Flemion®, and Aciplex® are most commonly used today in numerous industrial processes throughout the world.[1] However, because of their high cost, low stability at higher temperatures, and low gas-barrier property of these membranes, chemists have spent many decades in a continuing search for cheaper but higher performance electrolyte membranes.

One of the membranes investigated is formed by the modification of fluoropolymers using the radiation grafting method.[2–4] This method allows introduction of active functional groups into the grafted polymer chains in films, which can be modified for desired purposes. The PEMs have been prepared by the radiation grafting of styrene derivatives, such as styrene, vinyltoluene, and divinylbenzene into polymer films, followed by sulfonation with chlorosulfonic acid ($ClSO_3H$).[5–7] A PEM with a styrylsulfonic acid structure in grafted chains has less thermal and oxidative durability under fuel cell operating conditions because of the lower stability of aromatic sulfonic acid and the α-proton of polystyrene.

Recently, we successfully synthesized PEMs consisting of alkylsulfonic acid in grafts, by radiation-

induced graft polymerization of methyl acrylate (MA) into a poly(ethylene-co-tetrafluoroethylene) (ETFE) film followed by the sulfonation of MA units in the grafts using an equimolar complex of chlorosulfonic acid and 1,4-dioxane (ClSO3H-Complex).[8] It has also been confirmed that the sulfonation reaction was accompanied by equimolar decarboxylation of the MA units to the substituted sulfonic acids (substitution of carboxylic acid with sulfonic acid). However, the sulfonation reaction proceeds in about 30% of the units; as a result, 70% of the acrylic acid units, which has the methine proton at an α-carbonyl carbon, were remained in the grafting chains. Thus, it is expected that the newly developed MA-grafted PEMs possesses thermal and oxidative stabilities similar to those of styrene-grafted PEMs.[8]

In this study, we aimed to prepare PEMs, consisting of MA and methyl methacrylate (MMA) in various ratios, grafted into ETFE films, to improve thermal and chemical stabilities as well as mechanical strength by replacing the remaining MA units with MMA units, which do not have an exchangeable α-proton of carbonyl in the grafts.

EXPERIMENTAL

Preparation of the electrolyte membranes

The process for PEMs preparation includes three steps. First, the ETFE films (Asahi Glass Co. Ltd., Japan, Aflex®, film thickness: 50 μm) were irradiated with doses of 10, 20, 30, and 40 kGy using γ-rays from a ^{60}Co source under an argon atmosphere at room temperature, the monomer mixture of MA and MMA with volume fractions of 1 : 1, 2 : 1, 3 : 1, 5 : 1 and 10 : 1 (v/v) were then added and grafted into ETFE films in argon gas at 60°C for various times intervals. After graft polymerization, the grafted ETFE films were washed with a large amount of toluene to remove the homopolymers and residual monomers. Grafting degrees were calculated from the following equation, $(W_g-W_0)/W_0 \times 100$, where W_0 and W_g are the film weights before and after the grafting, respectively. Finally, the co-grafted membranes were sulfonated using the complex of equimolar (0.2M) chlorosulfonic acid and 1,4-dioxane in dichloroethane for 6 h.

Characterizations of the electrolyte membranes

The ion exchange capacity (IEC) was determined by titrimetric analysis. The dried membranes in the protonic form was immersed in 20 mL of NaCl saturated aqueous solution and equilibrated for 24 h. The residual solution was then titrated with a 0.02M NaOH solution using an automatic titrator (Hiranuma Com-555). Based on the titration results, IEC

was calculated by the following equation: [IEC (mmol/g)] = $(0.02 \times V_{NaOH})/W_d$, where V_{NaOH} (mL) is the titer of 0.02M NaOH solution and W_d is the dry weight of sulfonated membranes. The sulfonation degree (SD) (%) was calculated on the basis of monomer units of grafts consisting of MA and MMA. Sulfonated membranes were hydrated in water at room temperature for 24 h and then proton conductivity was obtained by impedance spectroscopy at room temperature using a Solartron 1269 analyzer. Water uptake of membranes was calculated from the following equation: [water uptake (%)] = $100 \times (W_w-W_d)/W_d$, where W_w is the weight of a membrane after immersing the dry membrane in deionized water at room temperature for 24 h and W_d is the weight of dried one, respectively. The weight of the membrane was measured gravimetrically after wiping excess water at its surface. The chemical stabilities were tested in a 3% H_2O_2 solution at 60°C and water at 80°C, separately. The membranes were immersed in the testing solutions and weighted after wiping excess water at its surface. The chemical stability was determined by durability time which is defined as the time required until the weight of the membranes decreased to less than 100% of the initial weight.

Analytical measurements of the electrolyte membranes

Fourier transform infrared (FTIR) spectroscopy of the ETFE film, grafted ETFE films and sulfonated films were measured with an FT-710 spectrometer (Horiba Ltd., Japan) equipped with a diamond attenuated total reflectance (ATR) cell. The thermal properties were characterized by differential scanning calorimetry and the thermogravimetric analysis of membranes using Thermo Plus 2/DSC8230 (Rigaku, Japan) calorimeter. The specimen of ca. 5 mg was heated up to 600°C at a heating rate of 10°C/min in nitrogen with a flow rate of 100 mL/min. The mechanical properties were determined using an STA-1150 universal testing instrument (A&D Co., Ltd, Japan) at a constant crosshead speed of 50 mm/min. Five specimens with a dumbbells shape were prepared according to ASTM D 1882-L and were used for the measurement.

RESULTS AND DISCUSSION

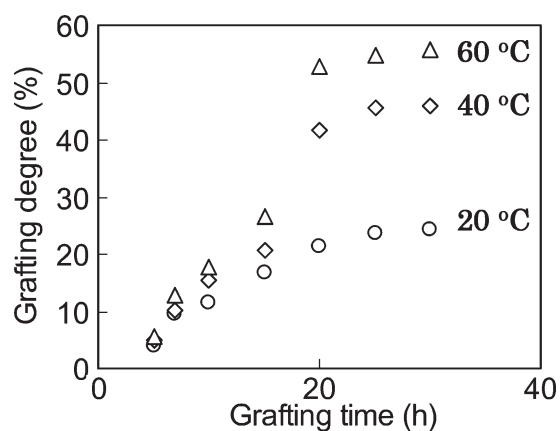### Graft copolymerization of MA and MMA with a ratio of 1 : 1

ETFE films were preirradiated with doses ranging from 10 to 40 kGy at a dose rate of 20 kGy h^{-1} and then graft copolymerization of MA and MMA at a feed ratio of 1 : 1 (v:v) was carried out at 60°C for 20 h. As shown in Figure 1, the irradiation of the film
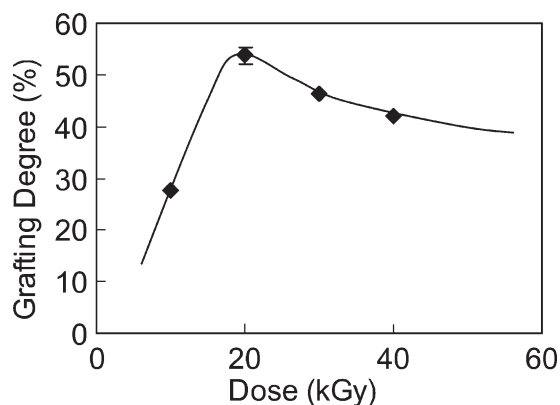
Figure 1 Effect of preirradiation dose on the grafting degree of copolymerization of MA and MMA (1 : 1 [v:v]) into a ETFE film at 60°C for 20 h.

with a dose of 20 kGy resulted in a grafting degree of 54%, which was higher than that irradiated with a dose of 10 kGy (28%). However, the grafting degree decreased to 46% and 41% with doses of 30 and 40 kGy, respectively. This effect of dose on the grafting degree can be explained by the crosslinking of radical sites with higher irradiation doses, which decreases the diffusion of monomers into trunk polymers, resulting in the decrease of grafting degree.[9] Thus, the optimal preirradiation dose for graft copolymerization over the crosslinking effects was determined to be 20 kGy.

Then, the effect of temperature on the grafting degree of MA and MMA into ETFE films preirradiated with 20 kGy was examined and the results were plotted in Figure 2. The grafting degrees gradually increased with increase in grafting time and leveled off after about 20 h at all grafting temperatures. At 60°C, the grafting degree increased quickly with increase in grafting time and reached a saturated value of 54% after 20 h. However, the grafting
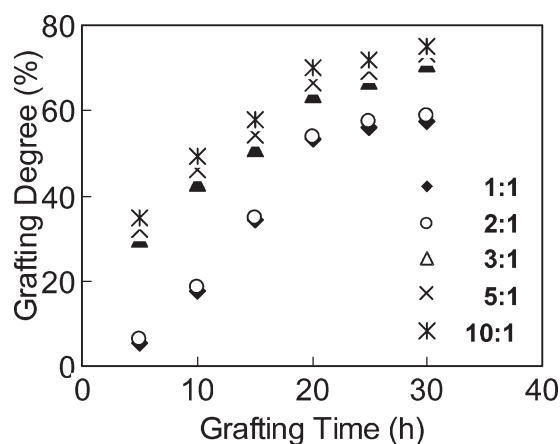
degrees at 20°C and 40°C reached only 24% and 42% even after 30 h, respectively. Accordingly, the increase in the grafting temperature up to 60°C brings about a significant increase in the maximum grafting degree. It had been reported that the increase in grafting degree at high temperature is due to the increase in monomer diffusion into polymer substrates, accelerating reactions between the monomer and the active sites of graft chain. However, it is well known that more homopolymers are generated at higher grafting temperatures.[10] Thus, we conducted grafting reactions at 60°C in subsequent studies.

## Graft copolymerization of MA and MMA in various ratios

The graft copolymerization of MA and MMA in feed ratios of 2 : 1, 3 : 1, 5 : 1, and 10 : 1 in addition to a 1 : 1 (v:v) into ETFE films preirradiated with a dose of 20 kGy was carried out at 60°C.

As shown in Figure 3, the grafting degrees increased gradually with increase in reaction time and reached saturated values after 20 h for all feed ratios. The saturated grafting degree is dependent on the composition of the two monomers. Specifically, with increase in MA content in the feed solution, the saturated grafting degree increased from 57% to 75%. There is a considerable increase in the total grafting degree with increase in MA content, especially with the increase in the feed ratios 3 : 1, 5 : 1, and 10 : 1 (v:v), whereas the grafting degree with the 2 : 1 feed ratio of MA and MMA seems to be similar to that with the 1 : 1 feed ratio. The increase in the grafting degree with increase in MA content is probably due to the reactivity of MA being higher than that of MMA in radical polymerization.

The molar ratios of the monomers of the grafts in ETFE films were calculated taking into consideration

Figure 2 Plots of the grafting degree of copolymerization of MA and MMA (1 : 1 [v:v]) into an ETFE film preirradiated with 20 kGy as a function of grafting time at 20°C, 40°C, and 60°C.

Figure 3 Plots of the grafting degree of copolymerization of MA and MMA with various feed ratios at 60°C with a dose of 20 kGy as a function of grafting time.
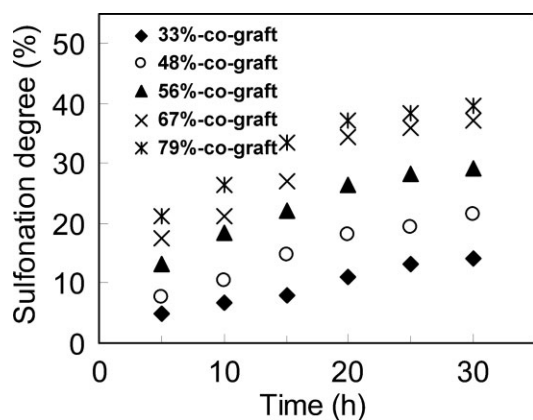
Figure 4 Relationship between sulfonation time and sulfonation degrees for the co-grafted ETFE samples with grafting time of 20 h in Figure 3. The sulfonation was conducted in 0.2M ClSO$_3$H-Complex in dichloroethane at 50°C.

the reactivity ratios of the two monomers in free radical copolymerization (r_1 [MA] and r_2 [MMA] derived from a radical copolymerization at 60°C are 0.34 and 1.69, respectively).[11] Given that the solubility or diffusion of the two monomers in the grafting region (mainly graft copolymers) are similar, the molar grafting ratio of each of the two monomers in the region of the films is not much different from their reactivity ratio in monomer solutions.[12,13] From the above reactivity ratios, the molar ratios of MA and MMA in the grafts of the grafted films prepared with feed ratios 1 : 1, 2 : 1, 3 : 1, 5 : 1, and 10 : 1 (v:v) were determined to be 33: 67, 48: 52, 56 : 44, 67: 33, and 79: 21, respectively. In this study, the grafted ETFE films with the above molar ratios are abbreviated to 33%-, 48%-, 56%-, 67%-, and 79%-*co*-graft ETFEs, respectively.

### Sulfonation of co-grafted ETFE with various ratios of MA and MMA

Recently, PEMs containing alkylsulfonic acid grafts were successfully synthesized by the substitution of carboxylic acid in MA-grafted ETFE films with sulfonic acid using an equimolar complex of chlorosulfonic acid and 1,4-dioxane (ClSO$_3$H-Complex). Thus, all the co-grafted films were treated in 0.2M ClSO$_3$H-Complex in dichloroethane at 50°C for 5, 10, 15, 20, 25, and 30 h.

Figure 4 shows the plots of SD of the sulfonated co-grafted films as a function of sulfonation time. The SD increased with the increase in sulfonation time and reached saturated values after 20 h. The dependence of the SD on the time may result from the increased swelling of membrane in solvent during prolonged reaction time, leading to the continuous diffusion of sulfonation reagents into a film. The

saturated SD of the grafted membranes increased from 14% to 39% when the MA content of the grafts increased from 33% to 79%. The increase in the SD with increase in the MA content in the grafted films is consistent with the fact that sulfonation can occur on the methine proton that is at the α position of carbonyl groups in an MA unit.[9] Furthermore, the maximum SD (39%) found in 79%-co-graft ETFE is in good agreement with the SD of about 30% in MA-grafted ETFE, which has MA homopolymer grafts. Therefore, the SD could be controlled by changing MA content in the feed solution.

The proton conductivity depends on the number of available strong acid groups, such as sulfonic acids, substituted into polymer grafts, and their dissociation capacity in water, which is accompanied by proton generation. Figure 5 shows the proton conductivity of hydrated membranes at room temperature as a function of IEC. The proton conductivity is almost proportional to the IEC; the 56%, 67%-, and 79%-*co*-graft ETFE membranes exhibited maximum proton conductivity of 0.068, 0.073, and 0.080 S/cm, respectively, which are the same level as the proton conductivity of Nafion 112.[14] It is known that proton conductivity or charge mobility occurs only in the presence of water, which interacts with the hydrophilic sulfonic acid groups (—SO$_3$H) substituted on the MA grafts surrounded by the hydrophobic matrix. This is the reason why the proton conductivity also depends on the molar ratio of MA and MMA in the grafts in an ETFE substrate.

The structural changes resulting from graft copolymerization of MA and MMA into an ETFE film and the subsequent sulfonation reaction of the grafted films with ClSO$_3$H-Complex were monitored by FTIR ATR measurement. Figure 6 shows the FTIR spectra of (a) the original ETFE film, (b) 33%-co-graft ETFE with grafting degree of 54%, and (c) sulfonated 33%-co-graft ETFE with SD of 16%.
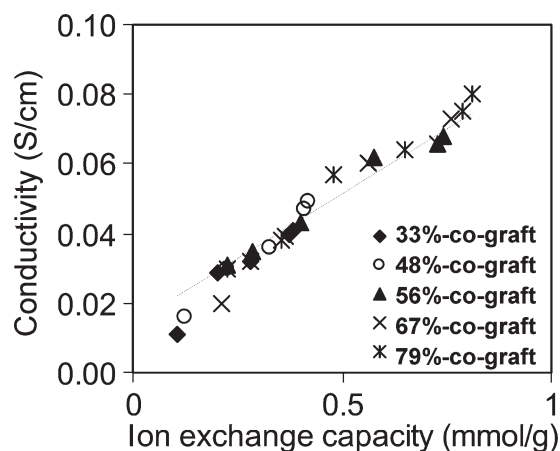
Figure 5 Plot of the proton conductivity as a function of IEC of the sulfonated co-grafted membranes.
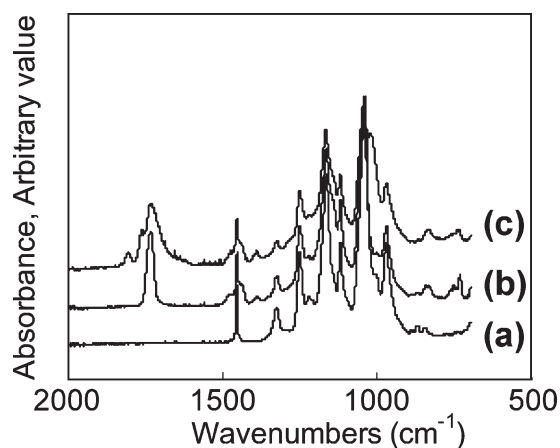
Figure 6 FTIR-ATR spectra of (a) original ETFE, (b) 33%-co-graft ETFE with a grafting degree of 54%, and (c) sulfonated 33%-co-graft ETFE with sulfonation degree of 16%.

Compared with the original ETFE film, the FTIR spectra of the grafted ETFE films had a new absorption peak at 1732 cm^{-1}, which is assigned to C=O stretching of MA and MMA units. The spectral change clearly indicates the incorporation of the two monomers into the ETFE film. After the sulfonation reaction, the peaks attributed to C=O stretching are broadened, probably because of the hydroxylation of ester (—COOR) into acid (—COOH) groups. A new peak, at 1035 cm^{-1}, is the characteristic of the stretching vibration of the O=S=O group, which results from the replacement of the carboxylic groups by a sulfonic acid on the MA unit in the copolymer grafts. These results confirm that the grafting and sulfonation of the membranes were successfully performed.

Chemical durability

The chemical stability of sulfonated membranes having similar proton conductivity in the range of 0.040 to 0.068 S/cm was evaluated in water at 80°C and in a 3% H_2O_2 solution at 60°C. The grafting degrees, SDs, and proton conductivities of the sulfonated co-graft membranes are listed in Table I. The index of

chemical stability was the durability time, which is defined as the time when the weight of the membranes decreased to less than 100% of the initial weight.

Since water molecules are generated at a cathode and are required for proton conductivity in PEMs during fuel cell operation, chemical stability of membranes was tested in water at 80°C, which was the typical operation temperature in a fuel cell. Figure 7(a) shows the change in the weight of membranes in water at 80°C as a function of time. The durability times of the tested sulfonated membranes in order of MMA content were 100, 94, 80, 68, and 58 h, respectively. As mentioned in the Introduction section, the sulfonation of MA units in MA homo-grafted membranes proceeds in just about 30% of the units; thus, more than half of the MA units remain in the grafts. Therefore, the sulfonated membranes with higher MMA contents possess fewer residual MA units after the sulfonation reaction, resulting in higher durability in water at 80°C.

The decomposition of membranes was also evaluated in a 3% H_2O_2 solution at 60°C, because the oxidative species HO•, which is generated during fuel-cell operation by oxygen diffusion through the membrane and incomplete reduction at a fuel-cell anode, can be formed by the thermal reaction of H_2O_2. These HO• radicals attack the hydrogen atom at an α-carbonyl carbon, leading to degradation of the copolymer grafts.[1] As shown in Figure 7(b), all membranes were initially stable for more than 50 h. However, the sulfonated 79%-, and 67%-co-graft ETFE membranes commenced decomposition after 53 and 82 h, whereas the sulfonated 33%-, 48%-, and 56%-co-graft ETFE membranes, which have fewer MA units, had longer durability times of 92, 104, and 115 h, respectively. As in the case of durability in water at 80°C, the sulfonated membranes with higher MMA content exhibited higher oxidative durability. These results clearly demonstrate that the replacement of MA units remaining after sulfonation with MMA units in copolymer grafts enhances the thermal and oxidative stability of the sulfonated membranes at higher temperatures.

TABLE I
Grafting Degrees (GD), Sulfonation Degrees (SD), and Proton Conductivities of the Sulfonated Co-Graft ETFE Membranes with the Molar Ratios of MA and MMA in the Grafts

No.	Feed Ratios (MA : MMA)	Molar Ratios (MA : MMA)	GD (%)	SD (%)	Water Uptake (%)	Conductivity (S/cm)
1	1 : 1	33 : 67	54	13	11	0.032
2	2 : 1	48 : 52	57	18	32	0.047
3	3 : 1	56 : 44	68	28	40	0.066
4	5 : 1	67 : 33	70	36	42	0.073
5	10 : 1	79 : 21	72	38	43	0.080
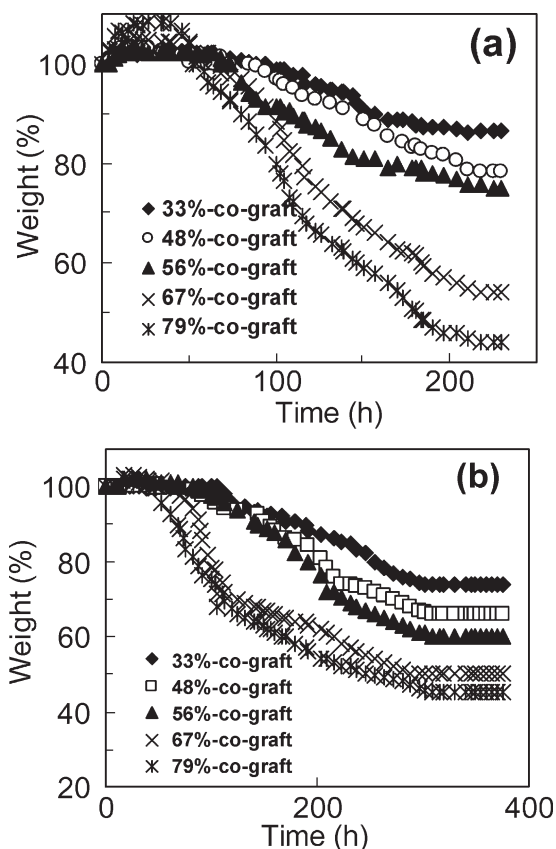
Figure 7 The change in the weight of the sulfonated co-grafted membranes as a function of time (a) in water at 80°C and (b) in H$_2$O$_2$ at 60°C.

Figure 8 Thermogravimetric analysis curves of (a) an original ETFE film (b) 79%-co-graft ETFE with a grafting degree of 70%, (c) sulfonated 79%-co-graft ETFE with a sulfonation degree of 39%.

Thermal and mechanical properties

The thermal and mechanical properties of PEMs have been studied extensively due to their practical importance in fuel-cell operation at elevated temperatures.[15] Thermal characterization of these films also provides fundamental information on polymer structure and properties. Figure 8 shows the thermogravimetric analysis profiles of (a) the original ETFE film, (b) 79%-co-graft ETFE with grafting degree of 70%, and (c) sulfonated 79%-co-graft ETFE with SD of 39%. In contrast with the original ETFE film, which was thermally stable up to 420°C, the 79%-co-graft ETFE with a grafting degree of 70% commenced degradation at around 250°C and exhibited two quite independent decomposition processes, in the range of 250°C to 420°C and above 460°C, characteristic of the degradation of the grafted chain and that of the ETFE base polymer. The sulfonated 79%-co-graft ETFE with an SD of 39% had additional weight loss starting at 250°C; thus, there were three weight loss steps, at 250°C to 310°C, 310°C to 420°C, and above 460°C, which can be assigned to originated from the desulfonation, thermal decomposition of grafted chains, and finally degradation of the ETFE

backbone, respectively. The comparison of these three membranes leads us to conclude that the sulfonation reaction exerts no distinct influence on the thermal stability of the grafted chain and the ETFE substrate.

The tensile strength and elongation at break of the original ETFE film, the ETFE film irradiated with a dose of 20 kGy, 79%-co-graft ETFE with a grafting degree of 70%, and sulfonated 79%-co-graft ETFE with an SD of 39% are listed in Table II. The preirradiation with a dose of 20 kGy slightly lowers both tensile strength and elongation at break of ETFE film from 58 to 53 MPa and from 460% to 410%, respectively. The 79%-co-graft ETFE has similar values (51 MPa, 390%), indicating that the grafting of these monomers does not affect these mechanical properties of the original ETFE film. The mechanical properties of the sulfonated 79%-co-graft ETFE membrane with an SD of 39% were much lower than the other membranes; the tensile strength and elongation at break were 41 MPa and 280%, respectively. Thus, the sulfonation reaction causes severe changes in the mechanical strength of the original and grafted films.

TABLE II
Tensile Strength and Elongation at Break of the Original ETFE Film, the ETFE Film Irradiated with a Dose of 20 kGy, 79%-Co-Graft ETFE with a Grafting Degree of 70%, and Sulfonated 79%-Co-Graft ETFE with a Sulfonation Degree of 39%

Films	Tensile Strength (MPa)	Elongation (%)
ETFE	58	460
Irradiated ETFE	53	410
79%-co-graft ETFE	51	390
Sulfonated 79%-co-graft ETFE	41	280

CONCLUSIONS

The PEMs with MA and MMA copolymer grafts that are 33%–79% MA units were prepared by preirradiation with a dose of 20 kGy and grafting in bulk comonomers at 60°C. The grafted membranes were treated with an equimolar complex of chlorosulfonic acid and dioxane (ClSO$_3$H-Complex) to obtain PEMs containing alkylsulfonic acid grafts. PEMs with IEC of 0.36-0.81 mmol/g (SDs of 20%–40%) and proton conductivity of 0.04 to 0.065 S/cm was obtained by changing the MA content, sulfonation occurring at an α-carbonyl carbon. PEMs with higher MMA content exhibited higher durability in water) (80°C) and under oxidative conditions (3% H$_2$O$_2$) at 60°C. This is probably because the co-grafted PEMs had fewer protons at an α-carbonyl carbon in the MMA unit, which are considered to be triggers of the degradation of grafting polymers.

References

1. Doyle, M.; Rajendran, G.Handbook of Fuel Cells, Fundamentals Technology and Applications, Vol 3: Fuel Cell Technology and Applications Part 1, Chapter 30: Perfluorinated membranes; John Wiley & Sons: West Sussex, 2003; p 351.

2. Hietala, S.; Holmberg, S.; Karjalainen, S.; Nasman, M. J.; Paronen, M.; Serimaa, R.; Sundholm, F.; Vahvaselka, S. J Mater Chem 2005, 7, 721.

3. Gubler, L.; Prost, N.; Gursel, S. A.; Scherer, G. G. Solid State Ionics 2005, 176, 2849.

4. Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. Prog Polym Sci 2003, 28, 1355.

5. Chen, J.; Asano, M.; Yoshida, M.; Maekawa, Y. J Appl Polm Sci 2006, 101, 2661.

6. Kang, K.; Kang, P. H.; Nho, Y. C. J Appl Polm Sci 2006, 99, 1415.

7. Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. J Appl Polm Sci 2006, 100, 4565.

8. Takahashi, S.; Okonogi, H.; Hagiwara, T.; Maekawa, Y. J Membr Sci 2008; 324, 173.

9. Chapiro, A.Radiation Chemistry of Polymeric System; Interscience Publishers; John Wiley & Sons: New York, 1962; Chapter XII.

10. Mayo, F. R.; Lewis, F. M. J Am Chem Soc 1944, 66, 1594.

11. Brandrup, J.; Immergut, E. H.Polymer Handbook; 2nd ed.; John Wiley & Sons: New York, 1975.

12. El-Naggar, A. M.; Zohdy, M. H.; Sahar, S. M.; Allam, E. A. Polym Int 2001, 50, 1082.

13. Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. J Membr Sci 2006, 269, 194.

14. Hübner, G.; Roduner, E. J Mater Chem 1999, 9, 409.

15. Benedetti, E.; Catanorchi, S.; D'allessio, A.; Moggi, G.; Vergamini, P.; Pracella, M.; Ciardelli, F. Polym Int 1996, 41, 35.