

# Effect of Crosslinkers on the Preparation and Properties of ETFE-Based Radiation-Grafted Polymer Electrolyte Membranes

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**ABSTRACT:** This study concerns a comparative study of three crosslinkers, divinylbenzene (DVB), 1,2-bis(*p,p*-vinylphenyl)ethane (BVPE), and triallyl cyanurate (TAC) crosslinked poly(ethylene-*co*-tetrafluoroethylene) (ETFE)-based radiation-grafted membranes, which were prepared by radiation grafting of *p*-methylstyrene onto ETFE films and subsequent sulfonation. The effect of the different types and contents of the crosslinkers on the grafting and sulfonation, and the properties such as water uptake, proton conductivity, and thermal/chemical stability of the resulting polymer electrolyte membranes were investigated in detail. Introducing crosslink structure into the radiation-grafted membranes leads to a decrease in proton conductivity due to the decrease in water uptake. The thermal stability of the

crosslinked radiation-grafted membranes is also somewhat lower than that of the noncrosslinked one. However, the crosslinked radiation-grafted membranes show significantly higher chemical stability characterized in the 3% H<sub>2</sub>O<sub>2</sub> at 50°C. Among the three crosslinkers, the DVB shows a most pronounced efficiency on the crosslinking of the radiation-grafted membranes, while the TAC has no significant influence; the BVPE is a mild and effective crosslinker, showing the moderate influence between the DVB and TAC crosslinkers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4565–4574, 2006

**Key words:** polyelectrolyte; membrane; irradiation; graft copolymerization; crosslinking

## INTRODUCTION

Fuel cell technology is considered to be one of the key energy conversion technologies of the future. Among the various fuel cell types, the polymer electrolyte membrane fuel cell (PEMFC), utilizing a polymer membrane as solid electrolyte for the proton transport and electrode separation, working at the temperature less than 200°C, is of particular interest as power sources in transport, stationary, and portable applications. Today, cost is the greatest challenge to PEMFC development to ensure commercial acceptance. The high cost is attributed to the need for expensive materials, i.e., platinum catalysts, corrosion resistant and high electric conductive separator, and perfluorosulfonic membranes. Considerable progress with respect to cost reduction has been achieved in past years, e.g., by reducing the platinum loading, by using the metal bipolar plates and the alternative polymer membranes.<sup>1</sup>

We focus our study on the development of the lower cost and higher performance alternative membranes for PEMFC. The main challenge in this field is

how to improve the chemical stability of the new type polymer electrolyte membranes. The membranes in a working fuel cell face a stringent condition such as high acidic and high temperature environment, oxidation and reduction reactions. These conditions will accelerate the degradation of the membranes, thus reducing the lifetime of the fuel cell. The perfluorosulfonic membranes, such as Nafion<sup>®</sup>, can withstand the extremely demanding conditions because of their high chemical stability. For example, the reported longest durability of PEMFC with perfluorosulfonic membranes as electrolyte is about 30,000 h.<sup>2</sup> However, the high cost of these perfluorosulfonic membranes limits their wide-scale industrial applications. Therefore, a major motivation of most of the more recent work in this field has been to find lower-cost and higher chemical stability membranes to replace the perfluorosulfonic membranes. Among these membranes being developed, radiation-grafted membranes have become attractive materials because of their high proton conductivity and relatively lower cost.<sup>3–24</sup> The longest durability of the PEMFC with the radiation-grafted membranes has reported to be 10,000 h,<sup>3</sup> and the price of the radiation-grafted membranes is considerably lower than that of the commercial perfluorosulfonic membranes. In addition, the radiation-grafted membranes have also been used in electro dialysis, elec-

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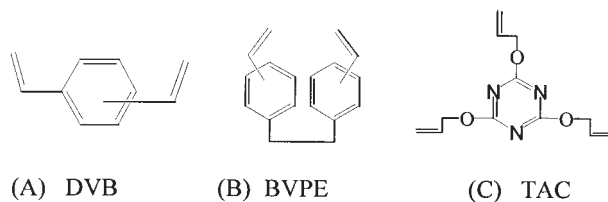
triosynthesis, protein extraction, and purification and recovery in etching processes.<sup>4,5</sup>

The radiation-grafted membranes are commonly prepared by radiation-grafting of styrene into various fluorinated polymer films followed by sulfonation. Radiation grafting can be performed by the preirradiation method or by simultaneous irradiation method.<sup>6</sup> The free radicals generated in the fluorinated films due to the irradiation initiate the graft polymerization. The sulfonation process gives proton conducting properties for the grafted films. Therefore, the process starts with a preformed commercial film and the preparation of the polymer electrolyte into thin membrane with uniform thickness is circumvented. The grafting kinetics, the correlations between the degree of grafting, and the physical properties of the resulting radiation-grafted membranes have been reviewed by Nasef and Hegazy.<sup>7</sup>

Crosslinking of the radiation-grafted membranes using multifunction monomer as a crosslinker during grafting reaction is an essential step towards the improvement in their chemical stability.<sup>8-11</sup> One of the most common crosslinkers is the divinylbenzene (DVB). The use of DVB as a crosslinker in the radiation-grafted membranes has showed significant influence on the properties of water uptake, proton conductivity, mechanical strength, and thermal/chemical stability.<sup>8-11</sup> It is also reported that crosslinking of the polymer electrolyte membranes can reduce the extent of fuel/gas permeability.<sup>11</sup> Despite the importance of DVB crosslinker to the chemical stability, a major challenge in handling these crosslinked radiation-grafted membranes have always been their rather poor mechanical properties and relatively low proton conductivity, especially in the case of the highly crosslinked membranes.

The method of radiation grafting also allows for further changes by choosing other monomers or crosslinkers to find membranes with improved properties. Chemically more stable but also more expensive membranes have been prepared at RAI Co. and Chlorine Engineers Co. by either simultaneous or preirradiation grafting of  $\alpha,\beta,\beta$ -trifluorostyrene onto base polymer films.<sup>12,13</sup> Chloromethyl styrene and  $\alpha$ -methylstyrene have been also studied as alternative monomers to increase the chemical stability.<sup>14</sup> In our recent study, *m,p*-methylstyrene (MeSt) was used as a new monomer to graft into poly(ethylene-co-tetrafluoroethylene) (ETFE) films.<sup>15</sup> The DVB crosslinked ETFE-*g*-MeSt polymer electrolyte membrane showed a considerably high chemical stability in comparison with the styrene-grafted one.

On the other hand, simultaneously introducing more than one type of crosslinker into the membranes has been demonstrated to be successful and leads to better membrane performances in fuel cells.<sup>8,9</sup> It is reported that the radiation-grafting membranes dou-



**Figure 1** Chemical structures of the crosslinkers used in this study. DVB, isomeric mixture of divinylbenzene; BVPE, 1,2-bis(*p,p'*-vinylphenyl)ethane; TAC, triallyl cyanurate.

ble-crosslinked with DVB and triallyl cyanurate (TAC) showed significantly high power density in the fuel cell.<sup>8</sup> The crosslinker of 1,2-bis(*p,p'*-vinylphenyl)ethane (BVPE) has also been reported in references.<sup>9</sup>

This study concerns the preparation of the radiation-grafted membranes for the potential application in PEMFC and the effect of crosslinkers on the preparation and properties of the membranes. For this purpose, the polymer electrolyte membranes were prepared by radiation grafting of MeSt into ETFE films and subsequent sulfonation; three crosslinkers, DVB, BVPE, and TAC, were used for the comparative study.

## EXPERIMENTAL

### Preparation of the radiation-grafted membranes

The preparation of the radiation-grafted polymer electrolyte membranes involves the preirradiation of the ETFE base films with  $\gamma$ -rays followed by graft copolymerization and sulfonation. The ETFE films (Asahi Glass Co., Japan) in the size of 2 cm  $\times$  3 cm  $\times$  50  $\mu$ m were added into a special reaction tube for the preirradiation. Prior to preirradiation, the reaction tube was degassed for 12 h and then filled with argon gas. Co-60 was used as the radiation source (Japan Atomic Energy Research Institute). The dose rate was 10 kGy/h and the total preirradiation dose was 20 kGy. After preirradiation, the films were immediately immersed in an argon gas-bubbled monomer solution containing 40 vol % *m,p*-methylstyrene (MeSt) (Aldrich) and crosslinkers, and 60 vol % toluene for the grafting reaction at 50°C under the oxygen-free atmosphere. Because of the excess of monomers relative to that consumed in the grafting and the absence of homopolymerization, the monomer concentrations in the grafting solutions were considered to remain relatively unchanged during grafting. Divinylbenzene (DVB) (55% isomeric mixture in ethylvinylstyrene, Fluka), 1,2-bis(*p,p'*-vinylphenyl)ethane (BVPE), and triallyl cyanurate (TAC) (Wako) showed in Figure 1 were used as the crosslinkers. The BVPE was synthesized according to the method described in Ref. 25 The crosslinker contents to the total monomers were in the ranges of 0–23 vol % for DVB, 0–67 vol % for BVPE,

and 0–38 vol % for TAC, respectively. The grafted films were then washed with toluene and dried under a vacuum before subsequent steps in membrane preparation. The degree of grafting was determined gravimetrically as  $(W_g - W_0)/W_0 \times 100\%$ , where  $W_0$  and  $W_g$  are the weights of the ETFE films before and after grafting, respectively.

The grafted films were converted into polymer electrolyte membranes by a sulfonation process. For this purpose, the grafted ETFE films were immersed into a chlorosulfonic acid solution at 25 or 60°C for designed time, hydrolyzed in deionized water at 80°C for 12 h. Thus, the new polymer electrolyte membranes consisting of the backbone chains of ETFE and the side chains of the sulfonated poly(MeSt) were obtained. It was washed and kept in deionized water at room temperature before use.

### Ion exchange capacity, proton conductivity, and water uptake

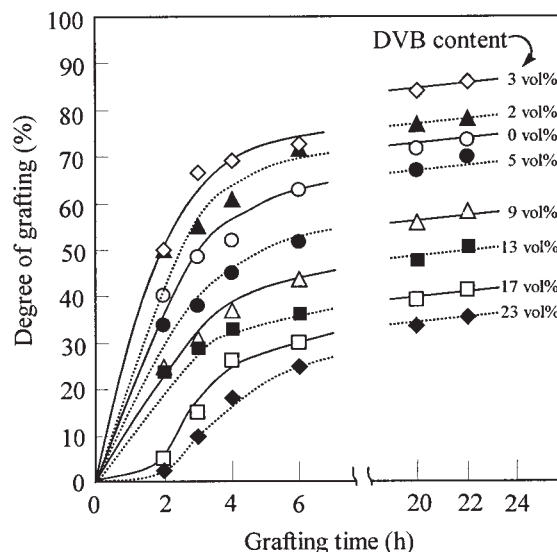
The ion exchange capacity was determined by acid–base titration. The dried membrane in the protonic form (about 80 mg) was immersed in 20 mL of NaCl saturated aqueous solution and equilibrated for 24 h. The solution was then titrated with 0.02M NaOH solution using an automatic titrator (HIRANUMA COM-555). On the basis of the titration results, the ion exchange capacity was calculated.

The proton conductivity at 25°C was obtained by impedance spectroscopy measurement using a Solartron 1269 analyzer with an AC perturbation of 10 mV. Prior to impedance measurement, the membrane was equilibrated with water at 25°C for 24 h. The membrane was clamped between two Pt clamps for recording the impedance spectroscopy. The membrane resistance was obtained by extrapolating the linear part of the spectra to the real axis of the impedance. The conductivity was calculated from membrane resistance, the area between the two Pt clamps and the membrane thickness.

The water uptake of the membrane, defined as the ratio of the weight of the absorbed water to that of the dry membrane, was determined by equilibrating the membrane with water. The dry weight was obtained after drying the membrane in a vacuum oven at 60°C. The wet weight was obtained by immersing the dry membrane in deionized water at 25°C for 24 h and weighing after wiping off the excess surface water. The water uptake was calculated as  $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$ , where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the wet and dry weights, respectively.

### Thermal and chemical stability

The thermal stability was determined by thermogravimetric (TG) measurement (type, Thermo Plus2/TG-



**Figure 2** Effect of DVB contents on the grafting kinetics of MeSt into ETFE films. Preirradiation, 20 kGy; grafting temperature, 50°C; monomer concentration, 40 vol %.

DTA, Rigaku, Japan). The specimen (about 5 mg) was heated at a heating rate of 5°C/min, with a nitrogen gas flow rate of 100 mL/min.

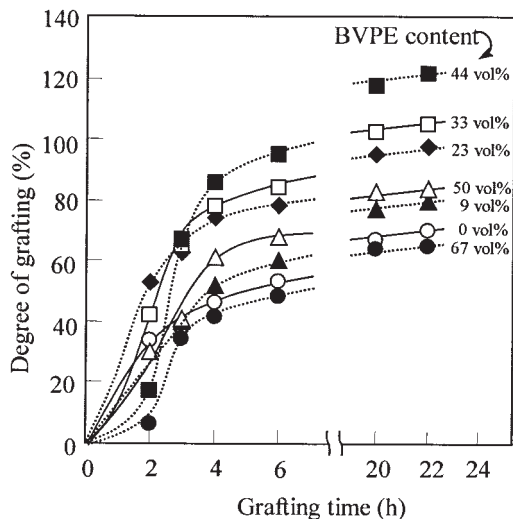
The chemical stability of the radiation-grafted membrane was characterized in a  $\text{H}_2\text{O}_2$  aqueous solution by tracking the weight change of the membrane.<sup>16</sup> For this purpose, the membrane with a size of  $2 \times 2 \text{ cm}^2$  was immersed in a 3%  $\text{H}_2\text{O}_2$  aqueous solution at 50°C. During the immersion, the membranes were intermittently taken out of the solution and then weighed after wiping the excess surface water.

## RESULTS AND DISCUSSION

### Effect of crosslinkers on the grafting

In our previous study,<sup>15</sup> we found that the degree of grafting in the membranes was strongly dependent on the grafting parameters, such as preirradiation dose, grafting time, and temperature, and the amount of crosslinker. The final degree of grafting increased with increasing the preirradiation dose and decreased with increasing the grafting temperature. Addition of 5 vol % DVB crosslinker increased the styrene grafting rate but decreased the MeSt grafting one.

In this comparative study, three crosslinkers, DVB, BVPE, and TAC, were used to crosslink the membranes. Radiation grafting of MeSt onto the 20 kGy-preirradiated ETFE films was carried out under the argon atmosphere at 50°C. The extent of crosslinking was controlled by varying the DVB, BVPE, or TAC contents in grafting solution. The grafting kinetics are shown in Figures 2–4, with the DVB in the range of 0–23 vol %, BVPE in the range of 0–67 vol %, and TAC



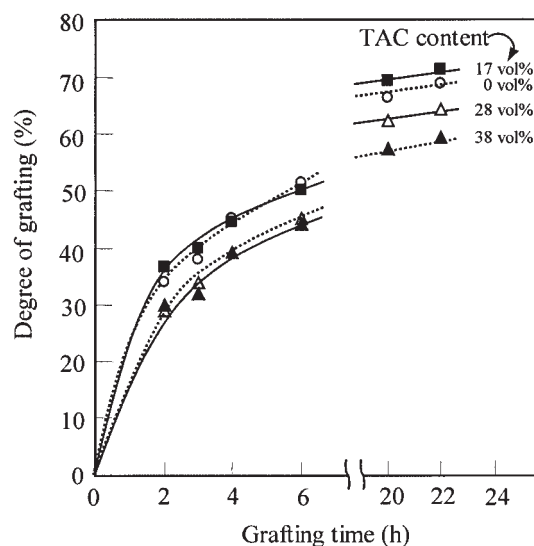
**Figure 3** Effect of BVPE contents on the grafting kinetics of MeSt into ETFE films. Preirradiation, 20 kGy; grafting temperature, 50°C; monomer concentration, 40 vol %.

in the range of 0–38 vol %, respectively. In all the grafting cases, the degrees of grafting initially increase gradually with time over a period of about 6 h, and then plateau out into gently sloping fairly linear region extending to 22 h.

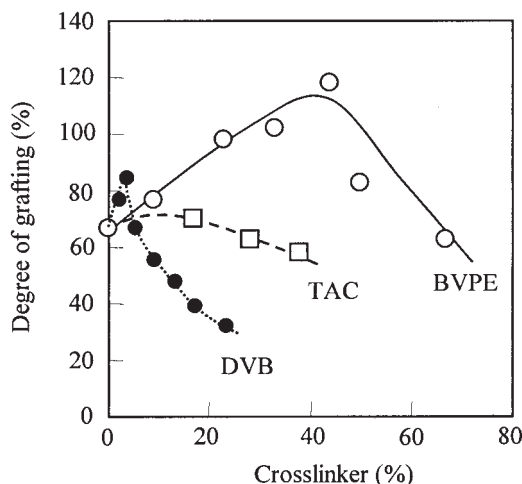
Obviously, the crosslinkers show a complex effect on the grafting of MeSt into ETFE films, acceleration or deceleration of the grafting reaction depending on the types and contents of the crosslinkers in the grafting solution.<sup>17,18</sup> For DVB crosslinker, as shown in Figure 2, lower contents of 2 and 3 vol % DVB in the grafting solution accelerate the grafting reaction, while higher contents of above 5 vol % DVB decelerate the graft reaction. This behavior can be explained by the grafting front mechanism.<sup>7</sup> ETFE films scarcely swell in the grafting solution and the initial grafting starts at the surface of the film only. The grafted layer swells in the grafting solution, allowing the monomer to diffuse to the next ungrafted layer and therefore more grafting proceeds by progressive diffusion of MeSt through the swollen grafted layer. In the case of lower DVB content, the accelerated graft reaction can be attributed to the higher activity of the DVB and the enhanced branching reaction. When one vinyl group of the DVB is reacted with a growing graft chain, another vinyl group is capable of polymerization with the other growing graft chain. On the contrary, the higher DVB content in monomer solution results in a tightly crosslinked graft structure on the film surface, which limits the mobility of the ETFE molecules and the graft chains, hinders the monomer diffusion to the next ungrafted layer. Thus, the graft reaction is decelerated. In addition, the inner radicals of base ETFE film may decay without contributing to the graft reaction. Therefore, there is a critical DVB content of about 3 vol % for the grafting reaction.

As shown in Figures 3 and 4, the behaviors of the effect of BVPE and TAC crosslinkers on the grafting kinetics were similar to that of the DVB crosslinker. However, in contrast to DVB, BVPE and TAC have been suggested as nonconjugated crosslinkers. The vinyl groups in the BVPE and TAC crosslinkers are electronically isolated from each other, and are thus expected to have identical reactivities to each other. The identical reactivities are expected to promise an almost random incorporation and homogeneous distribution of the crosslinkers in the grafted films. In addition, because of the flexibility and relatively long chain of BVPE and the star-structure of TAC, the introduced crosslink structure by the BVPE or TAC is considerably loose. The loose crosslink structure could hardly influence the diffusion of MeSt monomer into the ETFE base films. For this reason, as shown in Figures 3 and 4, the critical crosslinker contents for the BVPE and TAC, being 44 and 17 vol %, respectively, are significantly higher than that of the DVB. We also found that the BVPE crosslinked grafted films show the highest degree of grafting of about 120%. This is due to the higher reactivity of BVPE and its high content of 44 vol % in the grafting solution.

The effect of crosslinkers on the MeSt grafting is summarized in Figure 5, where the relationship between crosslinker content and the degree of grafting at the 20 h grafting time was plotted. For DVB and BVPE crosslinked films, the degrees of grafting are strongly depended on the crosslinker content. Especially for the DVB, the grafting is initially accelerated and then decelerated drastically in a large extent with the increase in DVB content. However, for the TAC, the effect on the grafting is not significant.



**Figure 4** Effect of TAC contents on the grafting kinetics of MeSt into ETFE films. Preirradiation, 20 kGy; grafting temperature, 50°C; monomer concentration, 40 vol %.



**Figure 5** Effect of different types and contents of the crosslinkers on the degree of grafting of MeSt into ETFE films. Preirradiation, 20 kGy; grafting temperature, 50°C; grafting time, 20 h; monomer concentration, 40 vol %.

The degree of crosslinking (ratio of crosslinker to total monomers) in the grafted films is different from the composition of the grafting solution, owing to the different reactivities and different diffusion coefficients of MeSt and crosslinkers in the films during the grafting process. It would have been of interest to know the crosslinker content in the membranes in addition to the content in the solution. We tried this determination by infrared spectroscopy and Raman spectroscopy, but unfortunately, such determinations were failed to give even semiquantitative results. In addition, the analysis of the crosslink distribution in the membranes is also experimentally difficult. However, it can be conjectured that the degree of crosslinking increases with increasing the crosslinker content in the grafting solution, and the radiation-grafted films are more highly crosslinked in their near surface regions. Another complexity of the grafting is that the crosslinkers may be incorporated in the films even if only one vinyl group reacts. The unreacted vinyl groups in the grafted films may lower the chemical stability of the resulting polymer electrolyte membrane.

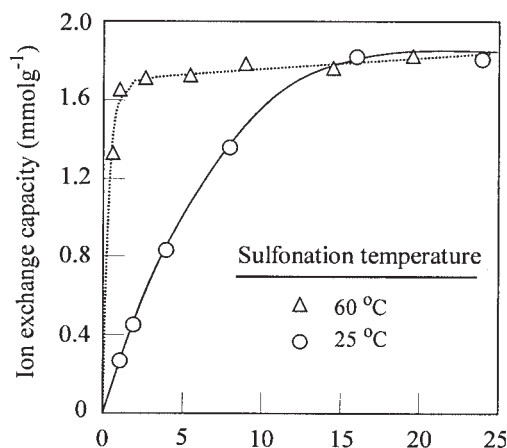
#### Effect of crosslinkers on sulfonation

Sulfonation of the grafted films was performed by immersing the films into chlorosulfonic acid solution and then hydrolysis in water. Preliminary experiments indicated that the hydrolysis condition of 12 h at 80°C is sufficient for converting all of the sulfonyl chloride into sulfonic acid groups. The ion exchange capacity, which provides an indication of the content of acid groups in the resulting membrane, was detected by the titration method.

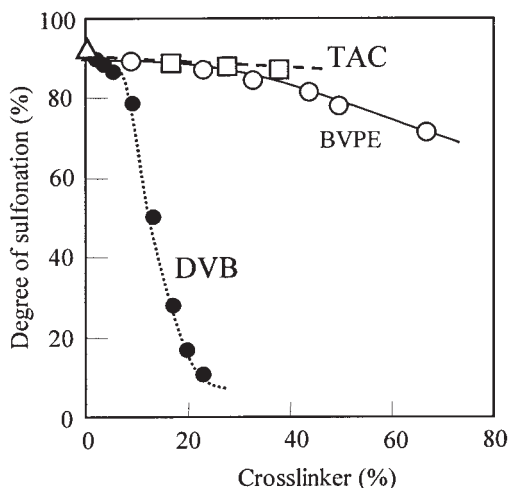
Figure 6 shows the ion exchange capacities of sulfonated ETFE-g-MeSt films (37% grafting, crosslinked with 3 vol % DVB) at 25 and 60°C, respectively, as a function of the sulfonation time. At lower sulfonation temperature of 25°C, the ion exchange capacity gradually increases up to 1.8 mmol/g at the sulfonation time of 16 h. On the other hand, the sulfonation reaction proceeds rapidly at higher sulfonation temperature of 60°C. For instance, at the initial 1 h, the ion exchange capacity reaches 1.7 mmol/g, and after that it is not significantly changed. It is considered that the sulfonation reaction is a diffusion-controlled process. The higher sulfonation temperature makes the films more swollen and accelerates the diffusion of chlorosulfonic acid into the films, resulting in a faster sulfonation.

The degree of sulfonation is defined as the ratio of experimental ion exchange capacity to the theoretical value. The theoretical ion exchange capacity is calculated by assuming one aromatic ring substituted by one sulfonic group, and assuming that the ratio of the monomer units in the graft chains is equal to that in the grafting solution. The theoretical ion exchange capacity of the afore-mentioned ETFE-g-MeSt film (37% grafting, crosslinked with 3 vol % DVB) is 1.9 mmol/g. Therefore, both the final degrees of sulfonation of the film under the two different sulfonation temperatures are over 90%. To ensure the grafted ETFE film to be sulfonated adequately, we choose the relatively violent conditions, i.e., sulfonation at 60°C for 8 h. Under this sulfonation conditions, the influence of the crosslinking on the degree of sulfonation has been investigated.

As shown in Figure 7, the noncrosslinked and lower crosslinked samples are sulfonated to a high degree over 90%. Samples crosslinked with high BVPE or TAC content are also sulfonated easily. On the other



**Figure 6** Effect of sulfonation time and sulfonation temperature on the ion exchange capacity of the resulting polymer electrolyte membrane.



**Figure 7** Effect of crosslinker content in the grafting solution on the degree of sulfonation of the resulting polymer electrolyte membrane. Sulfonation temperature, 60°C; sulfonation time, 8 h.

hand, the sulfonation of the DVB crosslinked films is strongly dependent on the degree of crosslinking. For the highly DVB crosslinked membranes, the degree of sulfonation was considerably lower. The incomplete sulfonation of the highly DVB crosslinked membranes can be explained by the tight crosslink structure, in which the diffusion of the chlorosulfonic acid to the reactive sites is hindered. On the contrary, crosslinking with BVPE and TAC resulted in a randomly and loose crosslink structure, which favors the sulfonation even in the case of high degree of crosslinking.

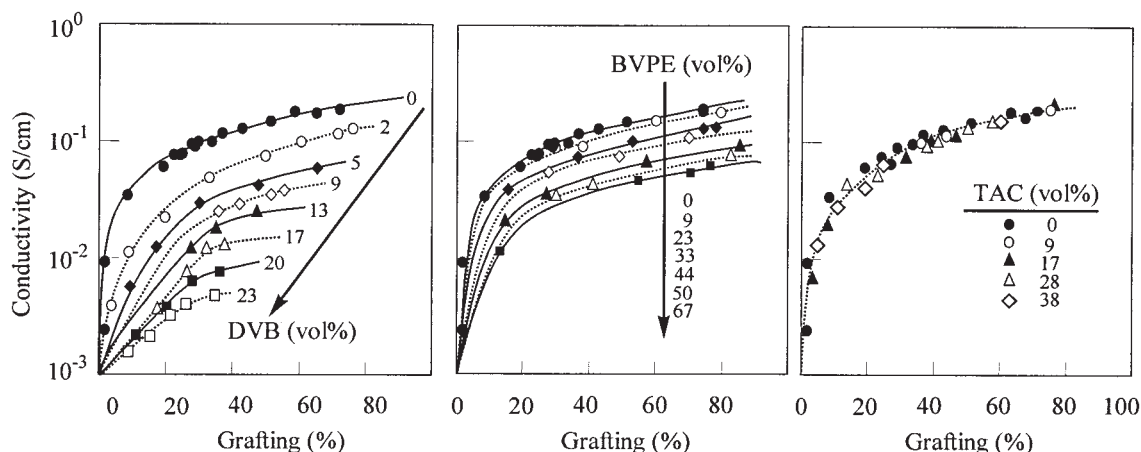
We also tried to sulfonate the highly DVB crosslinked samples under a more violent condition, such as 80°C for 24 h. Even then, the degree of sulfonation does not increase further. In addition, the highly DVB crosslinked and incomplete sulfonated membrane is considerably brittle.

### Effect of crosslinkers on the proton conductivity and water uptake

In polymer electrolyte membranes, the ion exchange capacity, water uptake, and proton conductivity are interrelated closely. This is also found to be the case with radiation-grafted membranes.<sup>9</sup> As a result of irradiation and subsequent grafting with MeSt and sulfonation, the originally hydrophobic and nonconductivity ETFE films are turned into water absorbing, proton conducting membranes. The proton conductivity of the resulting radiation-grafted membranes is of particular interest because of its relevance to the performance of the PEMFC where the membranes used as electrolyte. On the other hand, crosslinker is necessary in the radiation-grafted membranes to ensure the chemical stability. In addition, the crosslinker can also suppress the swell in aqueous phase and maintain the dimension stability of the membrane.<sup>9</sup>

As proton conductivity is related with the water uptake closely, we directly show the effect of crosslinker on the proton conductivity in Figure 8. The proton conductivity was determined at the water-saturated state at 25°C, which increases with increasing degree of grafting as expected. Figure 8 shows the results of the membranes crosslinked with DVB, BVPE, and TAC, respectively. The greatest proton conductivities, observed in the case of noncrosslinked, 9 vol % BVPE crosslinked, and TAC crosslinked membranes, were about 0.2 S/cm. It is far higher than that of the commercial perfluorosulfonic Nafion<sup>®</sup> 112 membrane, showing 0.06 S/cm under the same measurement conditions.

As shown in Figure 8, crosslinking with DVB resulted in a more pronounced decrease in the proton conductivity of the membranes at the same degree of grafting. For instance, at the degree of grafting about 40%, the proton conductivity of the noncrosslinked membrane is 0.12 S/cm and that of the 23 vol % DVB

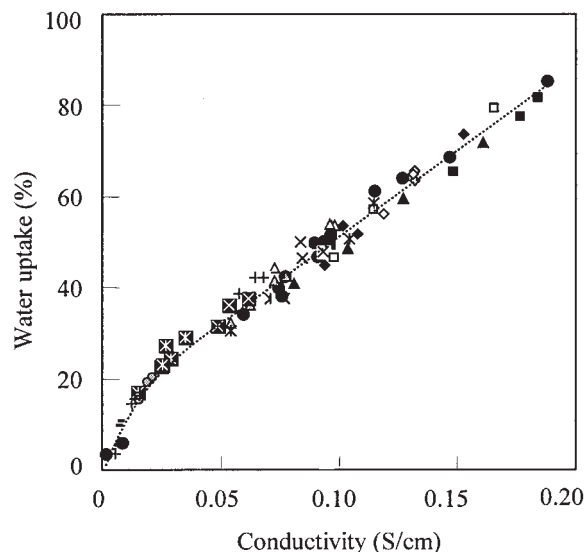


**Figure 8** Effect of different types and contents of the crosslinkers and the degree of grafting on the proton conductivity of the resulting polymer electrolyte membrane.

crosslinked membrane is only 0.006 S/cm. The significantly lower proton conductivity of the highly DVB crosslinked membranes is due to the extremely compact crosslink structure, which suppresses the water uptake, and partly due to the incomplete sulfonation. On the other hand, Lehtinen et al.<sup>9</sup> attributed the lower proton conductivity of the highly DVB crosslinked membrane to the higher graft penetration limit (defined as the lowest degree of grafting at which the graft chain is evenly distributed through the membrane), in which the incomplete graft penetration leads to the unfavorable distribution of the hydrophilic domains necessary for proton transport.<sup>19</sup>

The behavior of the BVPE crosslinked membranes is similar to that of the DVB crosslinked one (Fig. 8). However, the influence of BVPE content on the decrease in proton conductivity of the resulting membrane is somewhat lower. The 23 vol % BVPE crosslinked membrane at the degree of grafting of 40% shows a proton conductivity of about 0.08 S/cm, which is far higher than that of the 23 vol % DVB crosslinked membrane. On the other hand, as shown in Figure 8, the use of TAC crosslinker has no significant influence on the proton conductivity. The proton conductivity of the radiation-grafted membranes with and without the TAC crosslinker shows the same tendency. It was suspected that the TAC has incorporated into the membrane or the TAC has crosslinked the graft chain. However, the results of the slight enhanced grafting reaction at lower TAC crosslinker shown in Figure 4 and the increased chemical stability of the TAC crosslinked membrane described in the next section indicate that the TAC has really crosslinked the membrane. The lowest influence of TAC on the proton conductivity is most probably due to its special structure, i.e., longer side chains and ether functional group. The ether groups are known to render flexibility to the polymer because of their low rotational barrier. Therefore, the TAC crosslinks graft chains loosely, and the proton transport is hardly influenced by the crosslink structure.

It is well known that the radiation-grafted membranes swell considerably in an aqueous phase, depending on the degree of grafting and the types and contents of the crosslinkers. Swelling due to the water uptake decreases the mechanical strength and the dimension stability of the polymer electrolyte membranes, and increases the fuel/gas crossover. Introducing crosslink structure into the membranes can significantly decrease the swelling. However, the other important parameters, such as proton conductivity, should be taken into consideration. In Figure 8, we have shown that the proton conductivity decreases with increasing the crosslinker content. In Figure 9, the water uptakes of the synthesized membranes, without or with different types and contents of the crosslinkers, and the different degrees of grafting,



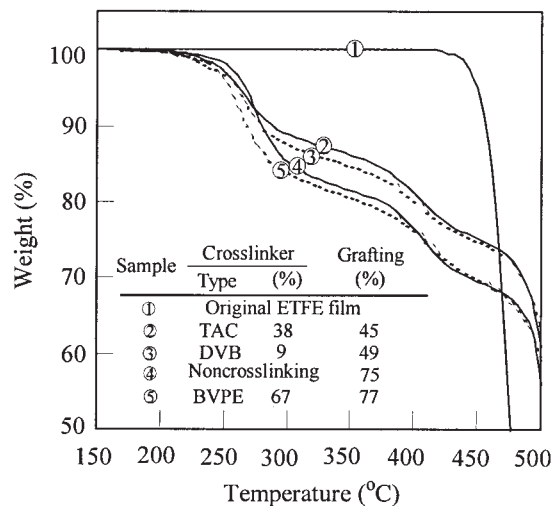
**Figure 9** Relationship between the proton conductivity and water uptake of the resulting polymer electrolyte membranes at 25°C. The different symbols indicate the membranes crosslinked with different types and contents of the crosslinkers.

were plotted as a function of proton conductivity. In this case, it was surprising that all the points, in spite of their different type and content of the crosslinkers, located around a curve showed in Figure 9. The curve composes two straight lines with different slopes. This is due to the different roles of the water in the membrane at the different conductivity level. At lower proton conductivity, adequate water is required for the formation of the ionic cluster and the tunnel for proton transport. On the other hand, at higher proton conductivity, the increase in water uptake widens the proton transport tunnel and increases the proton mobility.

From the relationship between proton conductivity and water uptake, the advantage of introduction of crosslink structure to the polymer electrolyte membrane is difficult to be confirmed. However, as we mentioned in the introduction section, the major virtue of the crosslink structure in the radiation-grafted membranes is due to their contribution to chemical stability, which is one of the most important problems that must be solved for the actual fuel cell application.

#### Effect of crosslinkers on the thermal and chemical stability

Thermal and chemical stability is one of the most important parameters of the membranes for fuel cells. The degradation mechanism of sulfonated polystyrene membranes in fuel cells has been addressed by Hodgdon et al.<sup>26</sup> more than 35 years ago. Weak links such as —O—O— bonds introduced by the polymer-



**Figure 10** TG curves of the original ETFE films and the different crosslinkers crosslinked radiation-grafted membranes.

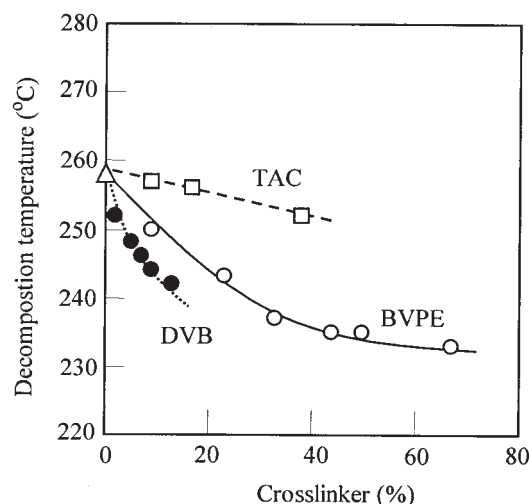
ization process and oxidative attack of  $\alpha$ -hydrogen by the HO radicals formed at the anode are postulated to be responsible for the degradation.<sup>27</sup>

Thermal stability of the radiation-grafted membrane was determined by TGA. The typical TGA results of (1) the original ETFE film, (2) the 38 vol % TAC crosslinked membrane (45% grafting), (3) the 9 vol % DVB grafted membrane (49% grafting), (4) the noncrosslinked membrane (75% grafting), and (5) the 67 vol % BVPE crosslinked membrane (77% grafting) are shown in Figure 10. The original ETFE film shows the highest thermal stability up to 420°C. However, for the radiation-grafted membranes (Fig. 10 (curves 2–5)), there appears three weight-loss steps in the temperature range of 200–500°C. The isolated three weight-loss steps at 240–310°C, 310–420°C, and above the 420°C are originated from the desulfonation, dearomatization, and finally the degradation of the ETFE backbone, respectively. The three isolated decomposition processes indicate that the synthesized membranes might be considerably inhomogeneous. We defined the thermal stability of the radiation-grafted membranes using the degradation temperature, where 2.5% weight loss occurred. Therefore, the degradation temperatures due to the desulfonation are 258, 253, 244, and 234°C for the noncrosslinked, 38 vol % TAC crosslinked, 9 vol % DVB crosslinked, and 67 vol % BVPE crosslinked membranes, respectively. Even then the crosslinkers are not favorable for the thermal stability, the degradation temperatures of the crosslinked radiation-grafted membrane are far higher than the temperature for the MEA preparation and the fuel cell operation.<sup>20</sup>

In our previous study,<sup>16</sup> we have reported that the degree of grafting has a strong effect on the weight loss in the membranes, but the degradation tempera-

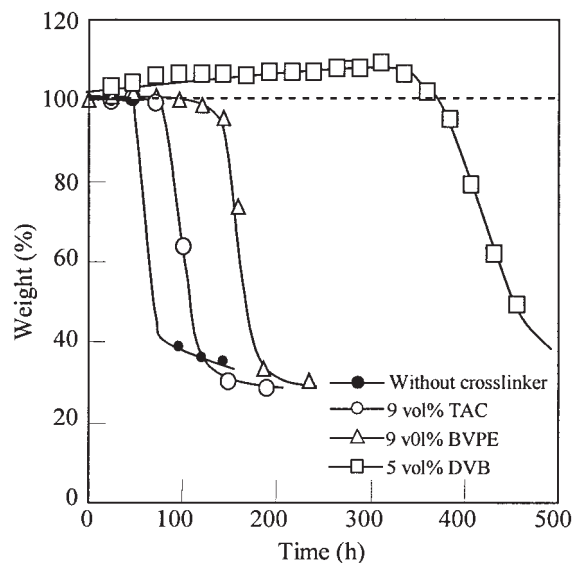
tures are shown to be independent of the degree of grafting. Therefore, the decrease in the thermal stability of the radiation-grafted membranes is due to the incorporation of the different types and contents of the crosslinkers. Figure 11 shows the effect of the different types and contents of the crosslinkers on the degradation temperature. Obviously, the thermal stability of the membranes decreases with the increase in the degree of crosslinking. The decrease in the thermal stability of the membranes is most probably due to the lower thermal stability of the crosslinkers. The influence of TAC on the thermal stability is not significant. This can be explained by the considerably lower activity of TAC, in which vinyl groups are nonconjugated with the aromatic ring directly, resulting in the significantly lower TAC content in the graft chains.

Chemical stability of the radiation-grafted membrane was characterized in a 3%  $H_2O_2$  solution at 50°C. Because of the slow thermal decomposition of  $H_2O_2$ , the HO radicals generated and accelerated the degradation of the electrolyte membrane. This environment is similar to that in a working fuel cell, where the  $H_2O_2$  is originated from oxygen permeated through the membrane and incomplete reduction at the anode. The weight of the membrane in the  $H_2O_2$  solution was determined as a function of time. Figure 12 shows the weight changes of the noncrosslinked (51.4% grafting), 9 vol % TAC crosslinked (73.1% grafting), 9 vol % BVPE crosslinked (60.2% grafting), and the 5 vol % DVB crosslinked (66.7% grafting) membranes. Chemical stability was defined by durability time where the outset of degradation (determined as a weight loss) appeared. Therefore, the durability times for the noncrosslinked, 9 vol % TAC crosslinked, 9 vol % BVPE crosslinked, and 5 vol % DVB crosslinked membranes are 48, 78, 132, and 368 h,



**Figure 11** Effect of crosslinker content on the decomposition temperature of the resulting polymer electrolyte membranes.





**Figure 12** Weight changes of the radiation-grafted membranes in the 3 wt %  $\text{H}_2\text{O}_2$  aqueous solution at  $50^\circ\text{C}$ .

respectively. Evidently, the crosslinked membranes were considerably chemically stable than the non-crosslinked membrane. Especially for the DVB crosslinked membrane, the durability is about seven times higher than that of the noncrosslinked one.

In addition, as shown in Figure 12, it is found that the DVB crosslinked membrane further swells initially about 10% in the  $\text{H}_2\text{O}_2$  solution. This behavior was not found in the noncrosslinked, TAC, and BVPE crosslinked membranes. As we mentioned earlier, the DVB crosslinks the membrane tightly, while the TAC and BVPE crosslink the membranes loosely. Therefore, the swelling of the DVB crosslinked membrane may be due to the continuous hydrolysis and the partial scission of the crosslink bonds in the  $\text{H}_2\text{O}_2$  solution.

Figure 13 shows the effect of different types and contents of the crosslinkers on the durability time of the radiation-grafted membrane. In comparison with the noncrosslinked membrane, the durability of the 9 vol % TAC crosslinked membrane is improved. However, further addition of TAC does not significantly improve the durability. On the other hand, the durability time of the BVPE crosslinked membrane linearly increases in a large extent, and reaches 280 h for the 67 vol % BVPE crosslinked membrane. The influence of DVB crosslinker on the durability is most pronounced. For instance, the durability time increases drastically even with small amount of DVB crosslinker, and in the range of 2–9 vol % DVB, the durability time is around 380 h. However, above the 9 vol % DVB, the durability time decreases drastically. The decrease in the durability time of the highly DVB crosslinked membrane is not very clear. We have mentioned earlier that the unreacted vinyl groups of DVB in the highly

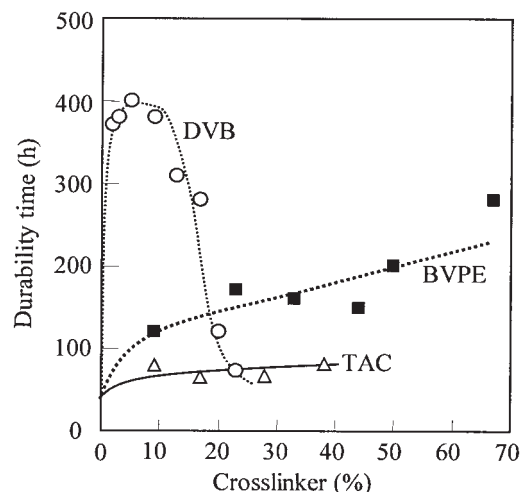
crosslinked membranes may decrease its chemical stability, because of the oxidation reaction with  $\text{H}_2\text{O}_2$ . The inhomogeneous crosslink distributions and the incomplete sulfonation in the highly crosslinked membranes may also be the reasons for the decrease in durability time.

The high chemical stability of the crosslinked membranes is not only due to the crosslinking of the graft chains, which is slowing down the loss of graft chain from the membranes, but also due to the reducing of the HO radicals diffusion into the membrane. In addition, highly crosslinked membranes can also decrease the oxygen permeation to the anode in a working fuel cell, and thus reduce the generation of the HO radicals. Consequently, the durability time of the polymer electrolyte membrane increases. In view of this point, relatively high DVB content in the grafting solution was recommended for the preparation of the crosslinked radiation-grafted polymer electrolyte membranes.<sup>8</sup>

## CONCLUSIONS

A comparative study of three crosslinkers, DVB, BVPE, and TAC crosslinked ETFE-based radiation-grafted membranes, has been made in this article. The radiation-grafted membranes were successfully prepared by  $\gamma$ -ray irradiation grafting ETFE films with MeSt and subsequent sulfonation in a 0.2M chlorosulfonic acid solution.

Addition of crosslinkers into the grafting solution either enhances or lowers the grafting depending on the types and contents of the crosslinkers. Lower crosslinker content enhances the grafting, while higher crosslinker content lowers it. The critical contents for the DVB, BVPE, and TAC are about 3, 44, and 17 vol %, respectively. The degree of sulfonation for



**Figure 13** Effect of crosslinker content on the durability time of the resulting polymer electrolyte membranes.

the noncrosslinked or lowly crosslinked membranes shows a high value of about 90%. However, for the highly crosslinked membranes, especially for the DVB crosslinked membranes, the degree of sulfonation decreases with increasing degree of crosslinking.

A common feature for the crosslinked membranes is the decrease in the conductivity, water uptake, and thermal stability, and the increase in the chemical stability. The highly DVB-crosslinked membranes are lower proton conductivity and brittle. In contrast, the highly BVPE and TAC-crosslinked membranes are higher proton conductivity and flexible. On the other hand, the influence of the crosslinker on the relationship between conductivity and water uptake is not significant, indicating that the decrease in proton conductivity of the crosslinked membrane is because of the decrease in water uptake. The thermal stability of the crosslinked membranes represented by desulfonation temperature is somewhat lower than that of the noncrosslinked one. However, the crosslinked membranes show significant chemical stability characterized in the 3% H<sub>2</sub>O<sub>2</sub> at 50°C. The noncrosslinked membrane shows a durability time of 48 h, while the 9 vol % TAC, 9 vol % BVPE, and 5 vol % DVB crosslinked membranes show the improved durability times of 78, 132, and 368 h, respectively.

From the comparative study, the DVB is the most effective crosslinker for the radiation-grafted membranes. However, highly DVB crosslinked membranes show low proton conductivity and bad mechanical properties. For this reason, a mixture of the crosslinkers with lower concentration of DVB and higher concentration of BVPE or TAC in the grafting solution is expected to be favorable for the synthesis of the membranes with high chemical stability and high proton conductivity, which has been the main subject in our further studies of the radiation-grafted membranes.

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