

# Radiation Grafting of $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(ethylene-Tetrafluoroethylene) Film by Preirradiation Method. III. Properties of Anion-Exchange Membrane Obtained by Chloromethylation and Quaternization of the Grafted Film

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## Synopsis

A study was made of certain properties of the anion-exchange membranes obtained by the preirradiation grafting of  $\alpha,\beta,\beta$ -trifluorostyrene (TFS) onto poly(ethylene-tetrafluoroethylene) (ETFE), followed by chloromethylation and quaternization of the grafted film. Swelling, water uptake, electric conductivity, and transport number of the membranes were measured as a function of ion-exchange capacity. Thermal and chemical stability were also investigated. These properties were found to be mainly dependent on ion-exchange capacity. The stable membrane properties were established due to a homogeneous ion-exchange group distribution in the membrane, as confirmed by X-ray microscopy analysis of the membrane cross sections. In addition, the membranes showed good electrochemical, thermal, and chemical properties, and were found to be acceptable for practical use as anion-exchange membranes.

## INTRODUCTION

Many attempts have been made to produce fluorine-containing cation-exchange membranes with high chemical and thermal resistance by radiation-induced graft polymerization. In particular, the grafting of hydrophilic monomers such as acrylic acid or styrene onto polytetrafluoroethylene (PTFE) films has been studied by many workers.<sup>1-4</sup>

Recently, fluorine-containing cation-exchange membrane has been prepared by the grafting of fluoro-containing monomers with functional groups onto polyethylene (PE), PTFE films, etc. Omichi et al., studying the grafting of methyl  $\alpha,\beta,\beta$ -trifluoroacrylate onto PE film and fluorine-containing films, found that hydrolyzed membrane shows good oxidation-resistance.<sup>5-7</sup>

In our previous works,<sup>8,9</sup> grafting of  $\alpha,\beta,\beta$ -trifluorostyrene (TFS) onto poly(ethylene-tetrafluoroethylene) (ETFE) film by the preirradiation method was attempted to produce a fluorine-containing cation-exchange membrane. The properties of the membranes obtained by sulfonation and hydrolysis of

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the grafted film were found to be acceptable for practical use as cation-exchange membranes.

However, the synthesis of fluorine-containing anion-exchange membranes by radiation-induced graft polymerization has been little reported. In the present study, a fluorine-containing anion-exchange membrane was synthesized by chloromethylation and quaternization of the grafted film which was obtained by the grafting of TFS onto ETFE film mentioned above. The electrochemical, swelling, thermal, and chemical properties, and the ion-exchange group distribution in the membrane were investigated to ascertain the possibility for practical application of the grafted membranes as fluorine-containing anion-exchange membranes.

## EXPERIMENTAL

### Membrane Synthesis

The grafted ETFE films were prepared by the preirradiation grafting method. The grafting procedure and properties of the monomer (TFS) and polymer substrate have been described in detail in our previous study.<sup>8</sup> The grafting conditions were as follows: preirradiation dose,  $1 \times 10^5$  Gy; monomer conc., 100%; grafting temp, 50°C; reaction time, 2–96 h; film thickness, 100  $\mu\text{m}$ . The grafted ETFE films were chloromethylated by immersion for 16 h at 85° in a solution consisting of 50 parts chloromethyl methyl ether and 50 parts 1,1,2,2-tetrachloroethane including aluminum chloride (0.68 mol/L). After washing with 2N HCl and drying, the chloromethylated films were immersed in benzene for 30 min at room temperature, and then quaternized by immersion in 30% trimethylamine solution for 6 h at reflux temperature. After washing with pure water and drying, the membranes were analyzed by infrared spectroscopy (IR-435, Shimazu Seisakusho Co.), X-ray microanalyzer, and elementary analyzer (240-B, Perkin-Elmer).

### Ion-Exchange Capacity

The ion-exchange capacity (IEC) was determined by the following method. The membranes were equilibrated in 1N NaCl at room temperature, boiled in distilled water to remove imbibed NaCl, and reequilibrated in 1N Na<sub>2</sub>SO<sub>4</sub> at room temperature. The displaced chlorine ions were titrated with 0.1N AgNO<sub>3</sub>.

### Other Measurements

The methods and apparatus used for the measurements of swelling behavior, electric resistance, transport number, thermal stability, and chemical stability were the same as those in our previous study of the cation-exchange membrane.<sup>9</sup>

## RESULTS AND DISCUSSION

### Membrane Synthesis

The grafting yield–time curves under the grafting conditions described in the experimental section were shown in our preceding paper.<sup>9</sup> Under experi-

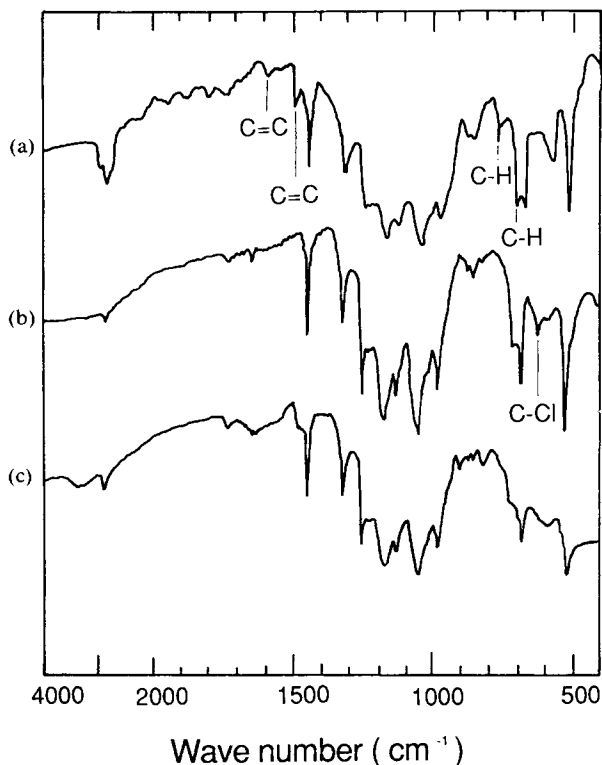


Fig. 1. Infrared spectra of the films: (a) grafted film (%G = 39.2); (b) corresponding chloromethylated film; (c) corresponding quaternized film.

mental conditions the grafting percentage could be altered up to approximately 50% by changing the reaction time.

Figure 1 shows the infrared spectra of the grafted film with 39.2% grafting yield, the corresponding chloromethylated film, and the corresponding film after quaternization. As discussed in our preceding paper,<sup>8</sup> monosubstitution of the aromatic ring was confirmed by the aromatic C—H deformation bands at 690 and 760  $\text{cm}^{-1}$ . After chloromethylation, the aromatic C—H deformation bands disappeared, and the absorption of C—Cl was observed at 610

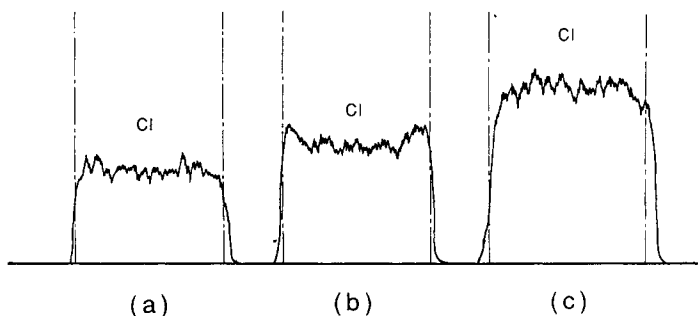
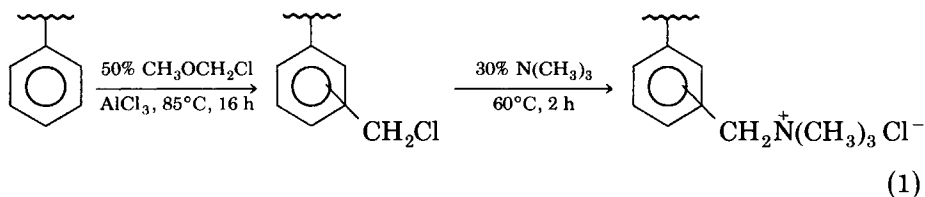


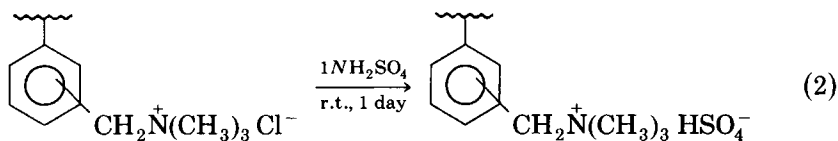
Fig. 2. Transversal distribution of chlor in the grafted membrane after the quaternization obtained by X-ray microanalyzer line profile measurement. Grafting yield: (a) 17%; (b) 21%; (c) 45%.

$\text{cm}^{-1}$ , confirming that the grafted film was chloromethylated. After quaternization the absorption of C—Cl disappeared, and the absorption of O—H stretching vibration of the absorbed water in the film was observed at  $3400 \text{ cm}^{-1}$ . The elementary analysis data showed the nitrogen contents of the chloromethylated and quaternized films to be below 0.01 and 1.33%, respectively. These features confirmed that the chloromethylated film was quaternized.

Figure 2 shows the chlorine distribution in the grafted chains after quaternization as measured by the line profile X-ray microanalysis. In this case, the chlorine distribution could correspond to the chlorine both of the unreacted chloromethyl group and the quaternary ammonium chloride as shown in



Therefore, the quaternized film was treated with  $1\text{N H}_2\text{SO}_4$  in order to convert the quaternary ammonium sulfate as shown in



After the sulfuric acid treatment, the chlorine peaks became negligibly small as shown in Figure 3. On the other hand, a homogeneous distribution of sulfur was observed, indicating that the chlorine distribution in Figure 2 corresponds to that of the quaternary ammonium chloride. In this grafting system, the ion-exchange group distribution over the membrane thickness is uniform at a grafting yield as low as 17%, and therefore can be expected to provide uniform membrane properties.

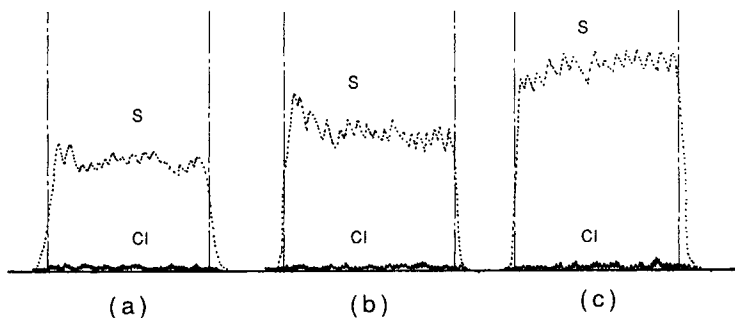


Fig. 3. Transversal distribution of chlorine and sulfur in the grafted membrane after the treatment in  $1\text{N H}_2\text{SO}_4$  obtained by X-ray microanalyzer line profile measurement. Grafting yield: (a) 17%; (b) 21%; (c) 45% (—) line profile chlorine; (---) sulfur.

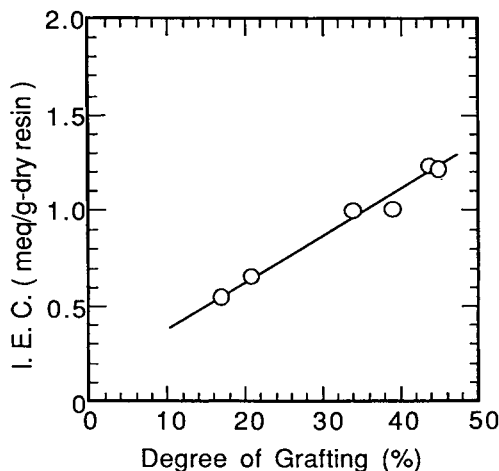


Fig. 4. Ion-exchange capacity vs. degree of grafting.

### Ion-Exchange Capacity

Figure 4 shows the relationship between the degree of grafting of the grafted film and the ion-exchange capacity. The ion-exchange capacity increases with the degree of grafting. As mentioned below, the membrane properties are largely dependent on the ion-exchange capacity; the selection of this capacity, therefore, controls the membrane properties. In this grafting system, the ion-exchange capacity can be widely altered by changing the degree of grafting, thus indicating that membranes having a wide range of properties can be prepared.

The degree of chloromethylation of the grafted film can be estimated in terms of ion-exchange capacity because the quaternization of the chloromethylated film was almost quantitatively achieved as previously described in the membrane synthesis section. For example, grafted film of a 45.3% grafting yield has IEC = 1.22 meq/g dry resin. Fully chloromethylated film of 45.3% grafting yield would have IEC = 2.20 meq/g dry resin, based on the moles of grafted TFS in the ETFE film. Using these figures, the degree of chloromethylation of the grafted film having a 45.3% grafting yield is calculated to be 55.5%.

### Swelling Behavior

Figure 5 shows the degree of water absorption against the ion-exchange capacity, and demonstrates that water absorption increases with ion-exchange capacity.

The water absorption of the grafted membrane (IEC = 0.99 meq/g dry resin) is 14.1%, which is lower than that of the Selemion AMV (IEC = 2.1 meq/g dry resin) figure of 24.3%. When the water absorption is represented as moles of absorbed water per an equivalent quaternary ammonium chloride group, the water absorption of the grafted membrane and Selemion AMV are 7.9 and 6.4 mol/eq quaternary ammonium group, respectively. As is well known, Selemion AMV is a typical hydrocarbon anion-exchange membrane synthesized by chloromethylation and quaternization of copolymer of styrene

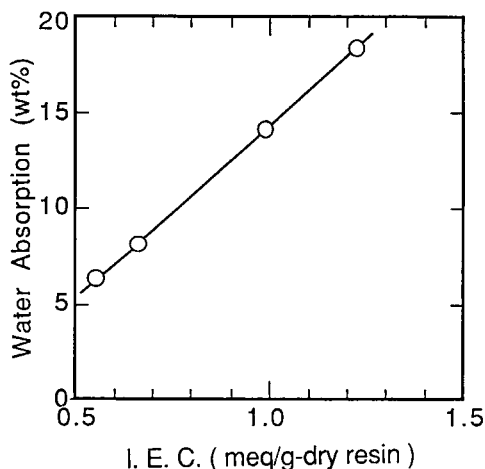


Fig. 5. Water absorption vs. ion-exchange capacity. The water absorption was measured in 0.6*N* KCl at 20°C.

and divinylbenzene having crosslinked structures and woven cloth backing. In the case of grafted membranes, the base polymer was not crosslinked. The structural differences between the grafted membrane and Selemion AMV seem to affect water absorption, but further investigation is necessary to clarify the relationship between membrane structure and water absorption.

Figure 6 shows the membrane length increase as a function of the ion-exchange capacity when the membranes are immersed in 0.6*N* KCl at 20°C. The linear expansion percent increases with the ion-exchange capacity; however, under experimental conditions the linear expansion percent of the grafted membrane is below 10%, demonstrating that the grafted membrane has a dimensional stability in a wet condition.

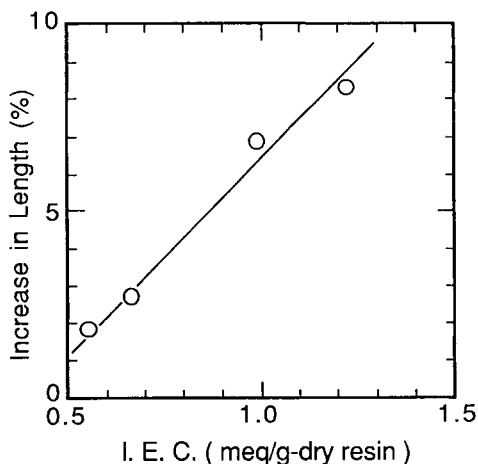


Fig. 6. Increase in length vs. ion-exchange capacity. The measurement conditions are the same as in Figure 5.

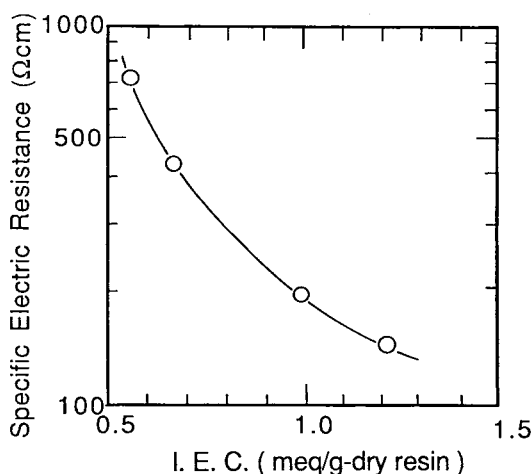


Fig. 7. Specific electric resistance vs. ion-exchange capacity. The measurement conditions are the same as in Figure 5.

### Electric Resistance

Figure 7 shows the relationship between specific electric resistance and ion-exchange capacity. The specific electric resistance of the grafted membranes decreased with the ion-exchange capacity. As described in our preceding paper,<sup>9</sup> the specific electric resistance of a grafted membrane is related to its ion-exchange group distribution in the membrane as well as the ion-exchange capacity. In this grafting system, the ion-exchange group distribution is homogeneous, as described in the membrane synthesis section. Therefore, the grafted membrane having low ion-exchange capacity shows relatively low specific electric resistance.

The specific electric resistance of the grafted membrane (IEC = 0.99 meq/g dry resin) is 197 Ω cm, lower than that of the Selemion AMV figure of 282 Ω cm. The ion-exchange capacity of the grafted membrane is almost half of the Selemion AMV (IEC = 2.1 meq/g dry resin); nevertheless, the specific electric resistance of the grafted membrane is lower because of its higher water absorption.

### Transport Number

Figure 8 shows the relationship between transport number and ion-exchange capacity. It can be seen that transport number decreases with ion-exchange capacity.

The transport number of the grafted membrane (IEC = 0.99 meq/g dry resin) is 0.93, showing that the grafted membrane has a high permselectivity. In general, the transport number is related to fixed ion concentration ( $A_w$ ) in the membrane, as defined by the following equation:

$$A_w \text{ (meq/g H}_2\text{O)} = A_r/W$$

where  $A_r$  and  $W$  represent the ion-exchange capacity (meq/g dry resin) and absorbed water in the membrane (g H<sub>2</sub>O/g dry resin), respectively. The

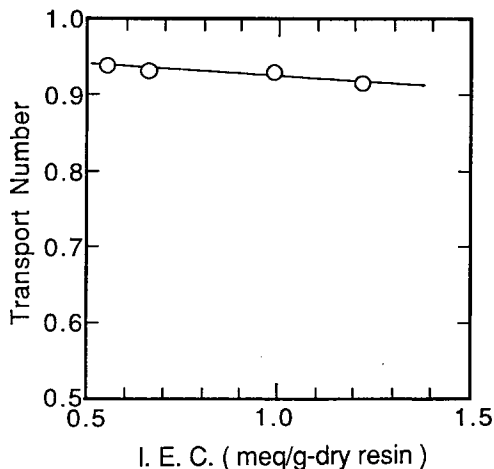


Fig. 8. Transport number vs. ion-exchange capacity. The transport number was measured in 0.5/1.0*N* KCl soln at 20°C.

transport number increases with the fixed ion concentration. The fixed ion concentration of the grafted membrane is 7.0 meq/g H<sub>2</sub>O, which is lower than that of the Selemion AMV figure of 8.6 meq/g H<sub>2</sub>O; therefore, the transport number of the grafted membrane (0.93) would be lower than that of the Selemion AMV (0.95).

### Thermal Stability

Figure 9 shows the degree of remaining membrane weight as a function of temperature. The ETFE film used for the grafting substrate starts to decompose at approximately 320°C. The weight of the grafted membrane (IEC = 0.67 meq/g dry resin) begins to decrease at over 50°C, which seems to be caused by

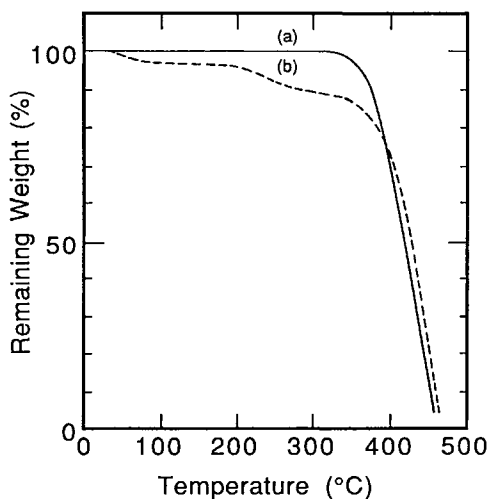


Fig. 9. Thermal decomposition of the base film and the grafted membrane: (a) ETFE film; (b) grafted membrane (IEC = 0.67 meq/g dry resin). TGA: heating rate, 5°C/min; atmosphere, air.



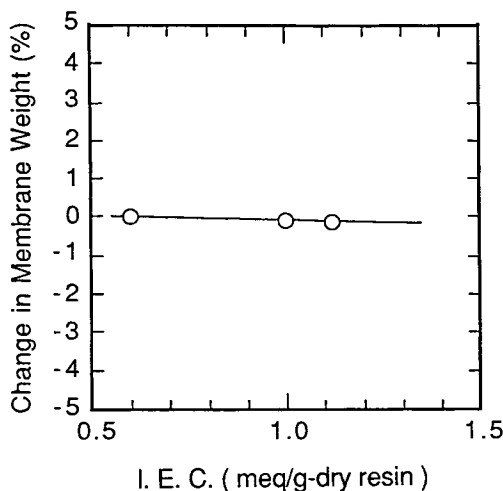


Fig. 10. Chemical stability of the grafted membrane. The grafted membranes were dipped in 3%  $\text{H}_2\text{O}_2$  soln ( $\text{Fe}^{2+}$ , 4 ppm) at  $70^\circ\text{C}$  for 5 h.

dehydration from the membrane. Moreover, the grafted membrane has two decomposition starting points at approximately  $200$  and  $320^\circ\text{C}$ . The second is in accord with that of the ETFE film; therefore, the first is supposed to be caused by the grafting chain decomposition.

### Chemical Stability

To investigate oxidation resistance, grafted membranes having various ion-exchange capacities were immersed in 3%  $\text{H}_2\text{O}_2$  solution in the presence of 4 ppm  $\text{Fe}^{2+}$  at  $70^\circ\text{C}$  for 5 h.

Figure 10 shows the degree of weight loss of the grafted membranes as a function of the ion-exchange capacity. The weight loss of the grafted membranes was negligible in experimental conditions.

The weight loss of the grafted membrane (IEC = 0.99 meq/g dry resin) is 0.1%, which is lower than that of Selemion AMV loss of 4.1%. These results indicate the effectiveness of fluorine-containing membranes in inducing high resistance to oxidative degradation.

### CONCLUSION

Investigation of the properties of grafted membranes, such as graft chain distribution, swelling behavior, electric resistance, transport number, and thermal and chemical stability, was made. It can be concluded that:

1. Infrared spectroscopy and elementary analysis of the grafted film after chloromethylation and quaternization confirmed the existence of quaternary ammonium chloride groups in the grafted membranes.
2. The distribution of the quaternary ammonium chloride group was observed by X-ray microanalyzer, confirming that its distribution was uniform throughout the membrane thickness.

3. The ion-exchange capacity of the grafted membranes can be widely altered by changing the degree of grafting, for example, from 0.55 to 1.22 meq/g dry resin under experimental conditions.
4. Both electric resistance and transport number of the grafted membranes are largely dependent on the ion-exchange capacity; therefore, the grafted membranes can be prepared for particular uses by selecting the optimum ion-exchange capacity.
5. The grafted membranes have two decomposition starting points at approximately 200 and 320°C.
6. The fluorine-containing membranes show good chemical stability as to oxidative degradation.
7. These aspects shown above demonstrate that grafted membranes have a possibility for practical use as anion-exchange membranes.

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