Radiation Grafting of α,β,β-Trifluorostyrene onto Poly(ethylene-tetrafluoroethylene) Film by Preirradiation Method. II. Properties of Cation-Exchange Membrane Obtained by Sulfonation and Hydrolysis of the Grafted Film

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Synopsis

A study was made on certain properties of the cation-exchange membranes obtained by the preirradiation grafting of α,β,β-trifluorostyrene (TFS) onto poly(ethylene-tetrafluoroethylene) (ETFE), followed by sulfonation and hydrolysis 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 cation-exchange membranes.

INTRODUCTION

A large effort has been devoted to the synthesis of ion-exchange membranes for brine and pure water electrolysis. Such membranes require high chemical and thermal resistance because they are used in contact with chlorine, oxygen, and alkaline solution at high temperatures. It has been established that only fluorine-containing membranes are durable under such severe conditions.[1,2] Until recently, the synthesis of perfluoro sulfonic and perfluoro carboxylic acid-type membranes were mainly studied using the catalytic copolymerization technique.[3-6]

Recently, the synthesis of fluorine-containing membranes has been studied by radiation-induced graft polymerization. Hegazy et al.[7] investigated the grafting of acrylic acid onto poly(tetrafluoroethylene) (PTFE) film, finding that the hydrolyzed membranes show good electrochemical behavior with mechanical properties similar to PTFE film. Omichi and Okamoto[8] studied the grafting of methyl α,β,β-trifluoroacrylate onto polyethylene (PE) film and fluorine-containing polymer films to find that the hydrolyzed membranes show good oxidation resistance.

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In the course of this study, we have investigated the kinetics of radiation-induced grafting of α,β,β-trifluorostyrene (TFS) onto poly(ethylene-tetra-fluoroethylene) (ETFE) film using the preirradiation method previously reported.[9] In the present study, properties of cation-exchange membrane obtained by sulfonation and hydrolysis of the grafted film, such as electrochemical, swelling, thermal, and chemical properties, and the distribution of ion-exchange group in the membranes, were investigated. The purpose of this study is to show the possibility for the practical application of grafted membranes as fluorine-containing cation-exchange membranes.

EXPERIMENTAL

Membrane Synthesis

The grafted PTFE films were prepared by the preirradiation grafting method. The grafting procedure and properties of the monomer (TFS), and the polymer substrate (ETFE) have been described in detail in our previous study.[9] The grafting conditions were as follows: preirradiation dose, 1×10^5 Gy; monomer conc., 100%; grafting temp., 50°C; reaction time, 2–96 h; film thickness, 100 μm. The grafted ETFE films were sulfonated by immersion for 20 min at 135°C in a solution consisting of 30 parts chlorosulfonic acid and 70 parts 1,1,2,2-tetrachloroethane. After washing with tetrachloroethane and drying, the sulfonated films were hydrolyzed by immersion in 2 N KOH solution for 2 h at 90°C. After washing with pure water and drying, the membranes were analyzed by infrared spectroscopy (IR-435, Shimazu Seisakusho Co., Ltd.) and by x-ray microanalyzer. As a comparison of the grafted membrane properties, the membrane properties of Nafion 110 were also investigated.

Ion-Exchange Capacity

The ion-exchange capacity (IEC) was determined by the following method; the membranes were equilibrated in 1 N HCl at 85°C, boiled in distilled water to remove embedded acid, and reequilibrated in 3 N Na$_2$SO$_4$ at 50°C. The displaced protons were titrated to a phenolphthalein endpoint with NaOH.

Swelling Behavior

Membranes of known weights were immersed in 0.6 N KCl solution at 20°C until equilibrium was reached, then removed. The excess solution on the surface of membrane was immediately removed by blotting paper and the films were then reweighed. The degree of water absorption was determined as follows;

$$\text{water absorption}(\%) = (W_s - W_g)/W_g \times 100$$

where W_g and W_s represent the weights of dry and wet membranes, respectively.

The membrane lengths were also measured before and after immersion in 0.6 N KCl to determine the dimensional changes caused by swelling.

Electric Resistance

The membranes were allowed to stand in 0.6 N KCl solution for 24 h at 20°C. Electric resistance was measured in 0.6 N solution at 20°C using an ohmmeter (LCR Meter 4261, Yokogawa-Hewlett Packard) working at 1000 Hz.

Transport Number

The membrane was conditioned in 0.5 N KCl solution for 24 h at 20°C and each was then inserted between two compartments to measure the electromotive force of the chemical cell. The solutions of 0.5 and 1.0 N KCl were made to flow individually through the compartments until equilibrium was reached, and the potential was measured at 20°C using an ion meter (Micro-Processor Ionanalyzer 1901 Orion Research). The transport number (t) of counter ions in the membrane was calculated from the value of the measured potential (E_m) by using the following equation;

$$t = E_m/E_o + 0.5$$

where E_o is the theoretical value of the potential calculated by Nernst equation;

$$E_o = (RT/F)\ln(C_2\gamma_2/C_1\gamma_1)$$

where γ_1 and γ_2 are the activity coefficients of KCl at concentrations C_1 and C_2, respectively.

Thermal Stability

The membrane of weight ~ 10 mg was heated from room temperature to 500°C in air at a heating rate of 5°C/min with thermogravimetry (TG-DSC 8085E1 Rigaku Denki).

Chemical Stability

The membranes were immersed in 3% H_2O_2 solution including 4 ppm Fe^{2+} at 70°C for 5 h. The membranes were then dried and weighed and the weight loss was calculated.

RESULTS AND DISCUSSION

Membrane Synthesis

Figure 1 shows the grafting percentage as a function of the reaction time. Under experimental conditions, the grafting percentage could be altered up to approximately 50% by changing the reaction time.

Figure 2 shows the infrared spectra of the grafted film with a 24.7% grafting yield, the corresponding sulfonated film, and the corresponding hydrolyzed membrane. As discussed in the previous study,[9] monosubstitution of the aromatic ring was confirmed by the aromatic CH deformation bands at 690 and 760 cm^{-1}. After sulfonation, the aromatic CH deformation bands disap-
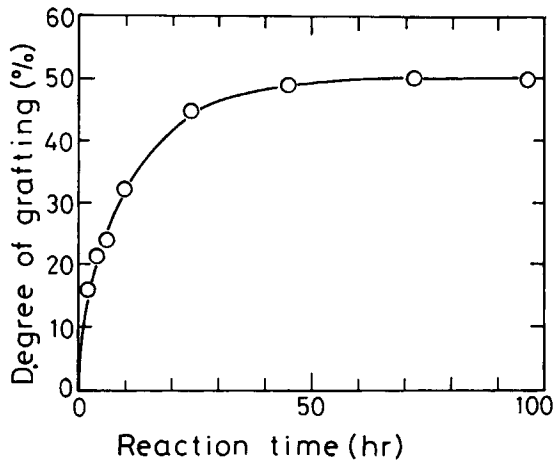
Fig. 1. Degree of grafting-time curve. Grafting conditions: preirradiation dose, 1×10^5 Gy; monomer conc., 100%; grafting temp., 50°C; film thickness, 100 μm.
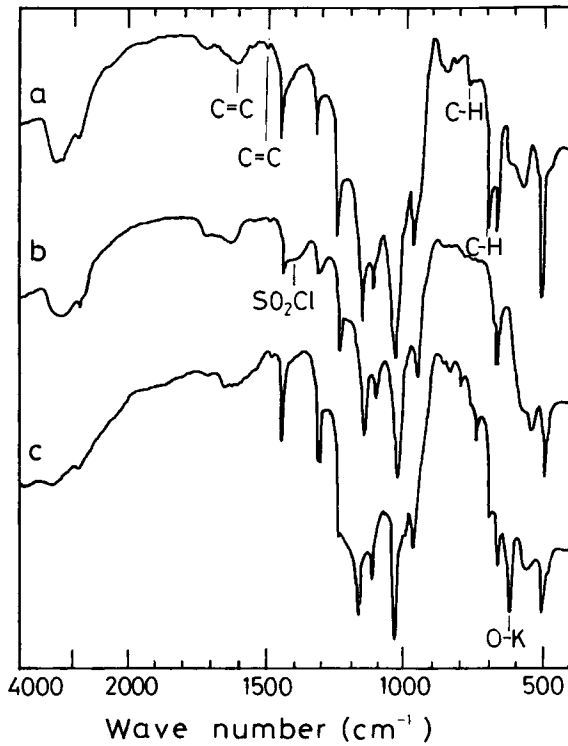

Fig. 2. Infrared spectra of the films: (a) grafted film (%G = 24.7); (b) corresponding sulfonated film; (c) corresponding hydrolyzed membrane.
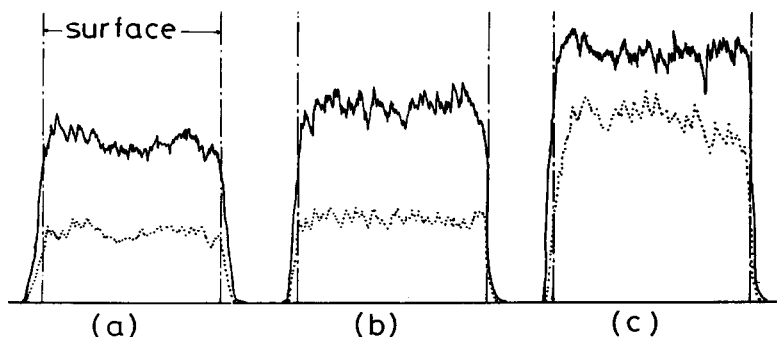
Fig. 3. Transversal distribution of sulfur and potassium in the grafted membrane after hydrolysis obtained by x-ray microanalyzer line profile measurement: grafting yield (a) 18%, (b) 34%, (c) 45%; line profile sulfur (——), potassium (- - - - -).

peared, and the broad absorption of SO_2Cl was observed at approximately 1400 cm^{-1}, confirming that the grafted film was sulfonated. The position of sulfonyl chloride group in the aromatic ring could not be determined by the infrared spectra; however, it is known that meta-substituted sulfonyl chloride is obtained in the sulfonation of poly-α,β,β-trifluorostyrene,[10] suggesting that meta-substitution of sulfonyl group will occur in the sulfonated grafted film. After hydrolysis, the absorption of SO_2Cl disappeared, and the absorption of O–K stretching vibration was observed at 620 cm^{-1}. These features confirm that the sulfonated film was hydrolyzed.

Figure 3 shows the sulfur and potassium distribution in the grafted chains after hydrolysis as measured by the line profile x-ray microanalysis. In this case, the distributions of both sulfur and potassium correspond to those of the potassium sulfate group ($-SO^-K^+$) as an ion-exchange group. One important requirement of an ion-exchange membrane is the homogeneous ion-exchange group distribution to establish uniform membrane properties. In this grafting system, the homogeneous distribution of ion-exchange groups in the whole bulk of membrane can be achieved at lower degree of grafting 18%, and it can be expected that such membrane provides uniform properties.

Ion-Exchange Capacity

Figure 4 shows the relationships between the degree of grafting and the ion-exchange capacity of the grafted film. The ion-exchange capacity increases with the degree of grafting. 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, consequently, membranes having a wide range of properties can be prepared.

The degree of sulfonation in the grafted film can be estimated in terms of ion-exchange capacity. For example, the grafted film having 50% grafting yield has an IEC = 1.68 mEq/g-dry resin. Fully sulfonated film of 50% grafting yield would have IEC = 1.86 mEq/g-dry resin, based on the moles of grafted TFS in the ETFE film. Using these figures, the degree of sulfonation in the grafted film having 50% grafting yield is calculated to be 90.3%.
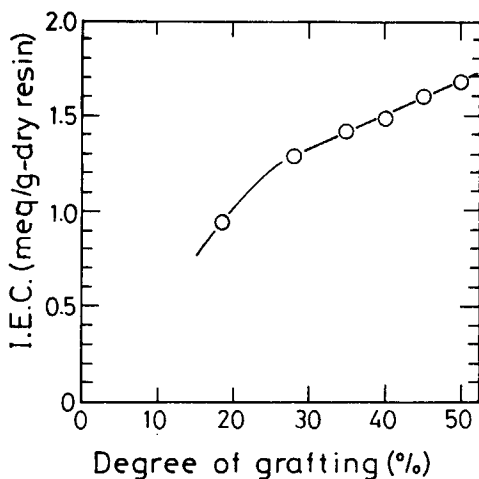
Fig. 4.   Ion-exchange capacity vs. degree of grafting.

Swelling Behavior

Swelling is largely associated with membrane electric resistance, transport number, and mechanical properties; therefore, swelling is an important characteristic of ion-exchange membranes. In this study, swelling of membranes having different grafting yields was investigated. 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 = 0.94 mEq/g-dry resin) is 8.3%, which is lower than that of Nafion 110 (IEC = 0.91 mEq/g-dry resin), 10.8%. When water absorption is represented as moles of absorped water per an equivalent sulfonic acid group, the water absorption of the
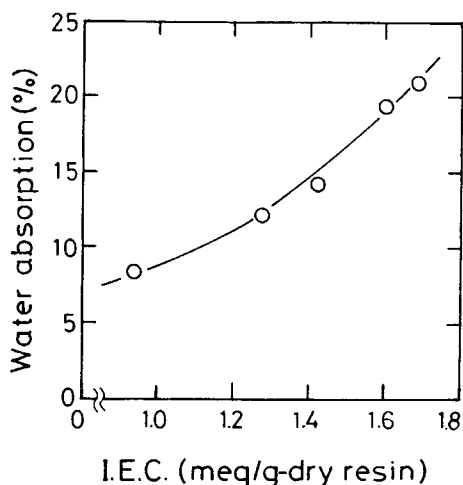

Fig. 5.   Water absorption vs. ion-exchange capacity. The water absorption was measured in 0.6 N KCl at 20°C.
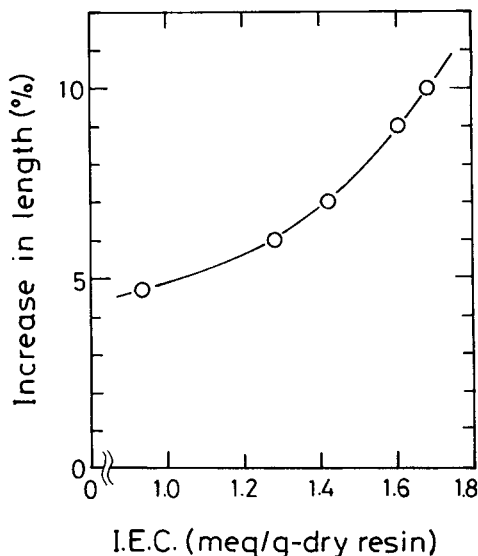
Fig. 6. Increase in length vs. ion-exchange capacity. The measurement conditions are the same as in Fig. 5.

grafted membrane and Nafion 110 are 4.9 and 6.8 mol/Eq sulfonic acid group, respectively. As is well known, Nafion 110 is a typical perfluoro sulfonic acid-type membrane synthesized by catalytic copolymerization of tetrafluoroethylene and perfluorovinyl ether having a sulfonic acid group. In the case of grafted membranes, the sulfonic acid groups are introduced to graft chains, but not to the base polymer. The differences in structure between the grafted membrane and Nafion 110 mentioned above seem to affect the water absorption, but further investigation will be necessary to clarify the relationship between membrane structure and water absorption.

Figure 6 shows the increase in membrane length 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% which is lower than the Nafion 110 figure of 10.8%, demonstrating that the grafted membrane has a dimensional stability in a wet condition comparable to Nafion 110.

Electric Resistance

Figure 7 shows the relationship between the specific electric resistance and the ion-exchange capacity of the grafted film. The specific electric resistance of the grafted membranes decreased linearly with the ion-exchange capacity. In general, the specific electric resistance of grafted membranes is related to the ion-exchange group distribution in the membranes as well as to the ion-exchange capacity. When there is a few ion-exchange group in the middle part of the membrane, the specific electric resistance is high, over 1×10^4 Ω cm, even if there are many ion-exchange groups on both membrane surfaces.[7] In this grafting system, the ion-exchange group distribution is
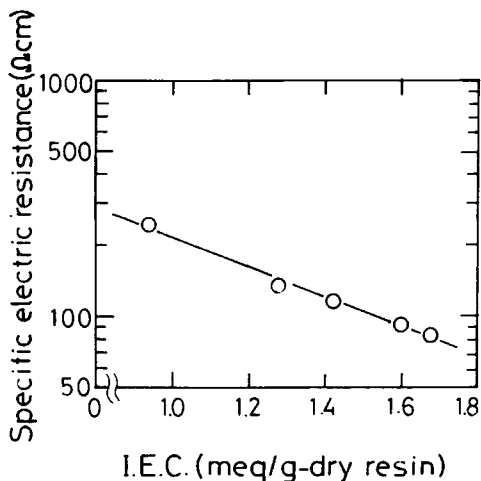
Fig. 7.   Specific electric resistance vs. ion-exchange capacity. The measurement conditions are the same as in Fig. 5.

homogeneous, as described in the membrane synthesis section. The specific electric resistance of the grafted membrane has, therefore, a linear relationship with the ion-exchange capacity.

The specific electric resistance of the grafted membrane (IEC = 0.94 mEq/g-dry resin) is 242 Ω cm, a little higher than that of the Nafion 110 figure of 166 Ω cm. In general, when the ion-exchange capacity is constant, the specific electric resistance of the membranes increases as the water absorption decreases. The water absorption of the grafted membrane is lower than that of Nafion 110, as described in the swelling behavior section. Therefore, it seems reasonable that the electric resistance of the grafted membrane is higher than that of Nafion 110.

Transport Number

Permselectivity is one of the most important properties of ion-exchange membranes. Therefore, the transport number of counter ions in the grafted membrane was measured.

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

The transport number of the grafted membrane (IEC = 0.94 mEq/g-dry resin) is 0.95 which is higher than that of the Nafion 110 figure of 0.92, that is, the grafted membrane has a high permselectivity compared with that of Nafion 110 at almost the same ion-exchange capacity. 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$_2$O/g-dry resin), respectively. The
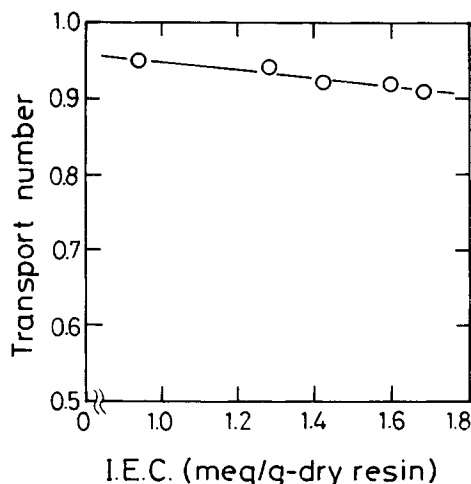
Fig. 8.   Transport number vs. ion-exchange capacity. The transport number was measured in 0.5/1.0 N KCl soln. at 20°C.

transport number increases as the fixed ion concentration increases. The fixed ion concentration of the grafted membrane (IEC = 0.94 mEq/g-dry resin) is calculated as 11.0 mEq/g-H_2O which is higher than that of the Nafion 110 figure of 8.2 mEq/g-H_2O; therefore, the transport number of the grafted membrane would be higher than that of Nafion 110.

Thermal Stability

Figure 9 shows the degree of remaining membrane weight as a function of temperature. The ETFE film which was used as a polymer substrate starts to decompose at approximately 320°C. The weight of the grafted membrane
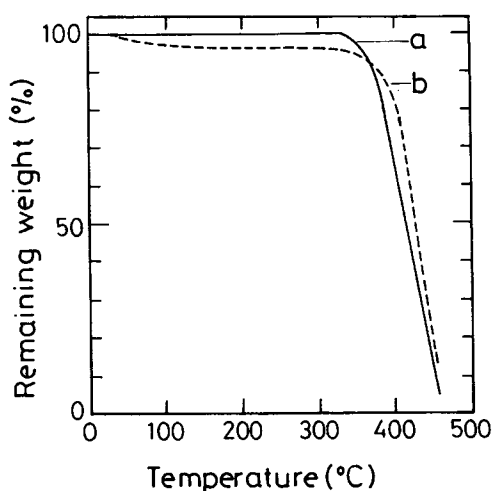

Fig. 9.   Thermal decomposition of the base film and the grafted membrane: (a) ETFE film, (b) grafted membrane (IEC = 1.2 mEq/g-dry resin). TGA: heating rate, 5°C/min; atmosphere, air.
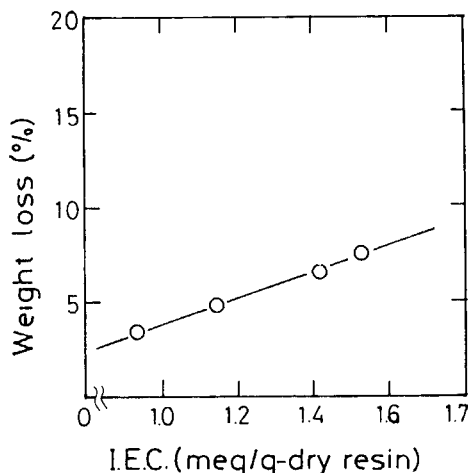
Fig. 10.   Chemical stability of the grafted membrane. The grafted membranes were dipped in 3% H_2O_2 soln. (Fe^{2+}, 4 ppm) at 70°C for 5 h.

(IEC = 1.2 mEq/g-dry resin) begins to decrease at temperature over 50°C, which seems to be caused by dehydration from the membrane. Moreover, the grafted membrane starts decomposing at approximately 320°C, which is in accord with that of ETFE.

Chemical Stability

To investigate oxidation resistance, grafted membranes having various ion-exchange capacities were immersed in 3% H_2O_2 solution in the presence of 4 ppm Fe^{2+} at 70°C for 5 h.

Figure 10 shows the percent of weight loss as a function of the ion-exchange capacity. The weight loss of the grafted membranes increased with the ion-exchange capacity.

The weight loss of the grafted membrane (IEC = 0.94 mEq/g-dry resin) is 3.4%, which is lower than that of acrylic acid-grafted polyethylene film[11] (grafting yield, 21%) loss of 17.4%. These results indicate the effectiveness of fluorine-containing membranes in inducing high resistance to oxidative degradation. However, the weight loss of Nafion 110 is 0.6%, which is lower than that of grafted membranes, indicating that fluorine-containing membranes are liable to oxidative degradation compared with perfluoro membranes such as Nafion 110. A further improvement in chemical stability of the grafted membrane might be necessary for applications requiring high oxidative degradation resistance, such as for chloralkali processes.

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 analysis of the grafted film after sulfonation and hydrolysis confirmed the existence of potassium sulfate groups in the grafted membranes.

2. Potassium sulfate group distribution was observed by x-ray microanalyzer, confirming that the potassium sulfate group 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 0.94 to 1.68 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 a decomposition starting point of 320°C, indicating high heat resistance.

6. The effectiveness of fluorine-containing membranes was confirmed in inducing resistance to oxidative degradation.

7. The aspects shown above demonstrate that grafted membranes have a potential for practical use as cation-exchange membranes.

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