

Radiation Grafting of α,β,β -Trifluoroethylenesulfonyl Fluoride onto Low-Density Polyethylene Film by Simultaneous Irradiation Method. II. Properties of the Grafted Membrane

TAKASHI MOMOSE,* ISAO ISHIGAKI, and JIRO OKAMOTO,
*Japan Atomic Energy Research Institute, Takasaki Radiation
Chemistry Research Establishment, 1233 Watanuki-machi,
Takasaki, 370-12 Japan*

Synopsis

Certain properties of the membranes obtained by simultaneous-irradiation grafting of α,β,β -trifluoroethylenesulfonyl fluoride (TFESF) onto low-density polyethylene (LDPE) were studied. Swelling, water uptake, electric conductivity, and transport number of the grafted membrane were measured; moreover, thermal and chemical stability were investigated. These properties were found to be mainly dependent on the degree of grafting. The electric conductivity and swelling of the membrane at less than ca. 25% grafting were found to be very low because the distribution of ion-exchange groups is heterogeneous as revealed by X-ray microscopy of the grafted films. At more than 25% grafting, the membranes showed good electrochemical and thermal properties, acceptable for the practical use as cation exchange membranes.

INTRODUCTION

Graft polymerization is a convenient means for the modification of chemical and physical properties of polymeric materials, especially for the preparation of various hydrophilic membranes.¹⁻⁴ Since interest in synthetic membrane is growing as an effective and economical means for the separation of molecular mixtures, radiation grafting of vinyl monomer onto polymer films has been extensively studied by many workers.

Recently, ion-exchange membranes with high chemical and heat resistance have been required for water electrolysis and caustic soda production. Hegazy et al.⁵ investigated the grafting of acrylic acid onto polytetrafluoroethylene (PTFE) film. They found that the hydrolyzed membranes show good electrochemical behavior with mechanical properties similar to PTFE film.⁵ Omichi et al., studying the grafting of methyl α,β,β -trifluoroacrylate onto polyethylene film and fluorine-containing films, found that the hydrolyzed membrane show good oxidation resistance.⁶

In the course of this study, we have studied the kinetics of radiation-induced grafting of α,β,β -trifluoroethylenesulfonyl fluoride (TFESF) onto low-density polyethylene (LDPE) by the simultaneous-irradiation method

*Present address, Chlorine Engineers Corp., Ltd., 2-1-1 Tranomon, Minato-ku, Tokyo, Japan.

reported previously.⁷ In the present study, the electrochemical, swelling, thermal, and chemical properties and distribution of ion-exchange group in the hydrolyzed membrane were investigated. The purpose of this study is to show a possibility for the practical application of the grafted membrane as ion-exchange membranes.

EXPERIMENTAL

Materials

The grafted LDPE films were prepared by the simultaneous-irradiation grafting method. The grafting procedure and properties of the monomer [trifluoroethylenesulfonyl fluoride (TFESF)] and polymer substrate (LDPE) have been described in detail in the previous study.⁷ The grafting conditions were as follows: dose rate, 1×10^4 Gy/h; monomer concn, 25% (*n*-hexane); grafting temp, room temp (ca. 20°C); grafting time, 6–90 h; film thickness, 50 μ m. The grafted films were hydrolyzed in 20 wt % KOH DMSO/water 1:2 solution for 4 days at temperature ranging from 90 to 100°C. After washing with pure water and drying, the membranes were analyzed by infrared spectroscopy (diffraction grating infrared spectrometer A-302, Japan Spectroscopic Co., Ltd.) and X-ray microanalyzer (JXA-Superprobe 773, Japan Electron Optics Laboratory Co., Ltd.).

Swelling Behavior

Membranes of a known weight were immersed in 2*N* KOH solution at 20°C until equilibrium was reached (24 h in most cases), then removed, and the excess solution on the surface was immediately removed by a blotting paper. The membranes were weighed again. The degree of water uptake was determined as follows:

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

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

Measurements of the membranes were made both before and after immersion to determine the dimensional changes caused by swelling.

Electric Resistance

The membranes were allowed to stand for 24 h at 20°C after being boiled in 2*N* KOH for 5 min. Electric resistance was measured in 2*N* KOH solution at 20°C using an ohm meter (LCR Meter 4261, Yokogawa-Hewlett Packard) working at 1000 Hz.

Transport Number

The membranes were conditioned in 0.5*N* KCl solution for 24 h at 20°C and then each was inserted between two compartments to measure the electromotive force of the chemical cell. 0.5 and 1.0*N* KCl solutions 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 counterions in the membrane was calculated from the value of the measured potential (E_m), using the following equation:

$$t = E_m/2E_0 + 0.5$$

where E_0 is the theoretical value of the potential calculated by Nernst equation

$$E_0 = (RT/F)\ln(C_2\gamma_2/C_1\gamma_1)$$

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

Thermal Stability

The membranes (ca. 10 mg) were heated from room temperature to 500°C in a nitrogen atmosphere at a heating rate of 10°C/min with a thermogravimetry (TG-DSC 8085E1 Rigaku Denki).

Chemical Stability

The membranes were immersed in 3% H₂O₂ solution including 4 ppm Fe²⁺ at 70°C for 5 h. After drying, the membranes were weighed, and the weight loss was calculated.

RESULTS AND DISCUSSION

Hydrolysis

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

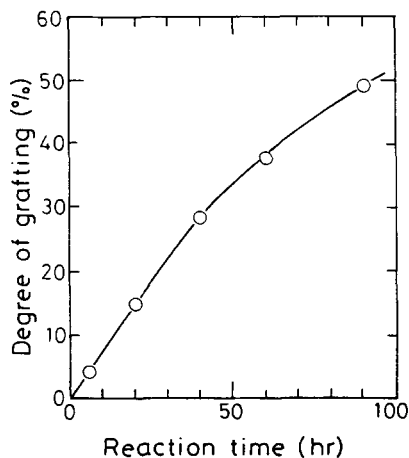


Fig. 1. Degree of grafting-time curve. Grafting conditions: dose rate, 1×10^4 Gy/h; grafting temp, 20°C; monomer concn, 25 vol %; film thickness, 50 μ m.

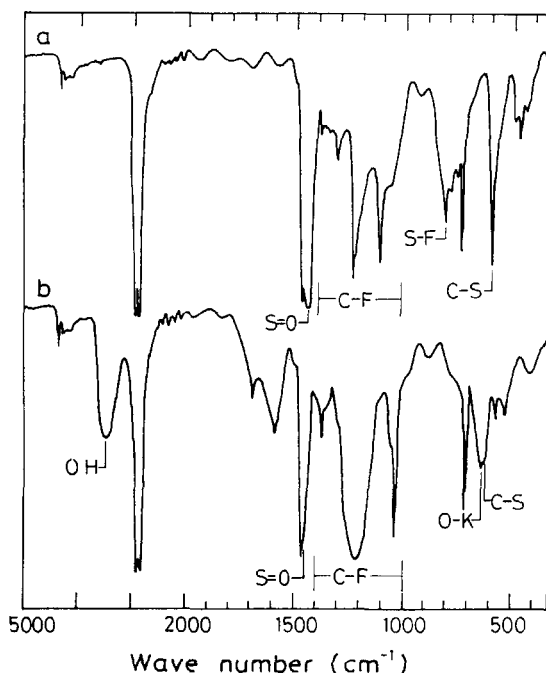


Fig. 2. Infrared spectra of the films: (a) grafted film (original LDPE film thickness $25 \mu\text{m}$; grafting percentage, 26.9%); (b) the corresponding hydrolyzed membrane.

Figure 2 shows the infrared spectra of grafted film with a 26.9% grafting yield and the corresponding membrane after hydrolysis. As discussed in the preceding paper,⁷ the sulfonyl fluoride group was established by the $\text{S}=\text{O}$ stretching vibration at 1440 cm^{-1} , the $\text{S}-\text{F}$ stretching vibration at 810 cm^{-1} , and the $\text{C}-\text{S}$ stretching vibration at 600 cm^{-1} . After hydrolysis the absorption of the $\text{S}-\text{F}$ stretching vibration disappeared, and the absorption of the $\text{O}-\text{K}$ stretching vibration was observed. The absorption at 3470 cm^{-1} was considered to be $\text{O}-\text{H}$ stretching vibration due to the absorbed water in the membrane. These features confirm that the grafted film was hydrolyzed.

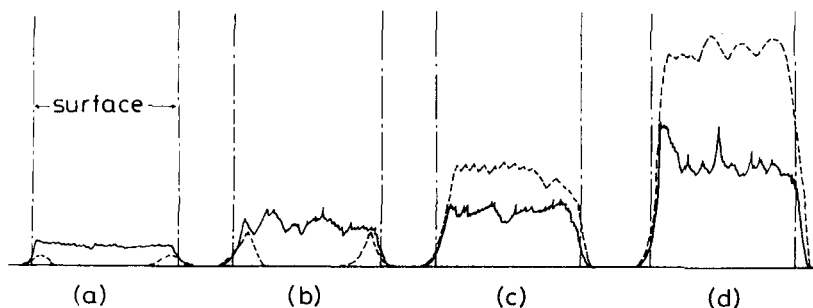


Fig. 3. Transversal distribution of sulfur and potassium in the grafted chains after hydrolysis obtained by measuring the line profile with X-ray microanalyzer; grafting percentage: (a) 4.5%; (b) 13.1%; (c) 26.2%; (d) 50.0%; (—) line profile sulfur; (---) potassium.

Figure 3 shows the distribution of sulfur and potassium in the grafted chains after hydrolysis measured by X-ray microanalysis of line profile. The distribution of sulfur corresponds to that of the grafted chains. On the other hand, the distribution of potassium corresponds to that of potassium sulfate groups obtained by hydrolysis. At a lower grafting percentage [Figs. 3(a) and 3(b)], the nonhydrolyzed layer still remains in the middle of the film. The nonhydrolyzed layer disappears as the grafting percentage increase [Figs. 3(c) and 3(d)]. Under the experimental conditions, it was found that the grafted film is hydrolyzed to the center of the film at a grafting percentage above ca. 25%.

Swelling Behavior

Swelling is one of the characteristics of grafted membranes due to the presence of hydrophilic groups. In this study, swelling of the membranes having different grafting percentage was investigated. Figure 4 shows the degree of water uptake against the grafting percentages. It can be seen that

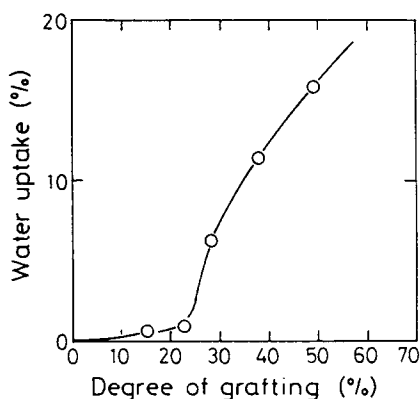


Fig. 4. Water uptake vs. degree of grafting. The water uptake was measured in 2N KOH soln at 20°C. Grafting conditions are the same as in Figure 1.

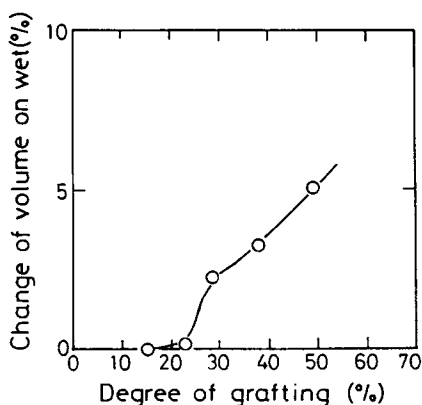


Fig. 5. Percent change of volume on wet as a function of degree of grafting. Percent change of volume was measured in 2N KOH soln at 20°C. Grafting conditions are the same as in Figure 1.

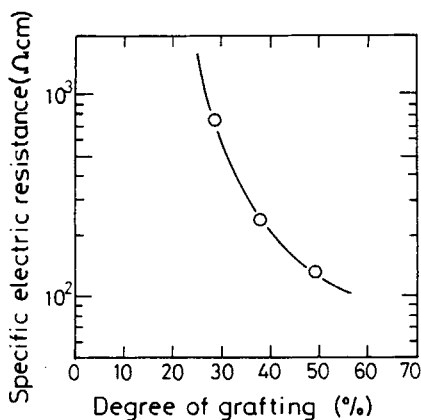


Fig. 6. Specific electric resistance vs. degree of grafting. The electric resistance was measured in 2*N* KOH soln at 20°C. Grafting conditions are the same as in Figure 1.

water uptake increases with grafting percentages. At a lower grafting percentage, only small amounts of water were absorbed, increasing rapidly when grafting percentages rose above ca. 25%.

Figure 5 shows the extent of swelling expressed as the percentage increase in volume ($\Delta V\%$) as a function of grafting percentage. In a similar manner as above, the volume increased rapidly when the grafting percentage rose above ca. 25%.

It can be suggested that swelling behavior of the grafted membrane changed rapidly when the grafted film was hydrolyzed to the center of the film.

Electric Resistance

Figure 6 shows the relationship between specific electric resistance and grafting percentage. At less than 25% grafting, the electric resistance was over $1 \times 10^4 \Omega \text{ cm}$, it dropped rapidly at around 25% grafting and continued to decrease as the grafting percentage rose. These results can be reasonably understood by the distribution of potassium sulfate groups through the membrane. In the region where the membrane has a higher electric resistance, the potassium sulfate groups do not exist at the center of the film. The abrupt fall in electric resistance of membrane can be explained by the fact that the potassium sulfate group reaches the center of film when grafting percentage exceeds ca. 25%.

Transport Number

The permselectivity of membrane is one of the most important properties of ion-exchange membrane. Therefore, the transport number of counterions in the grafted membrane were measured.

Figure 7 shows the relationship between transport number and grafting percentage. The membrane potential was approximately 0 mV at less than 25% grafting. The transport number increased rapidly at around 25% grafting, after that decreasing as the grafting percentage increased. It is supposed that, at lower grafting percentage, the nonhydrolyzed layer prevents the transmission of cation through the membrane. The permselectivity of the grafted membrane is confirmed, when grafting percentage exceeds ca. 25%.

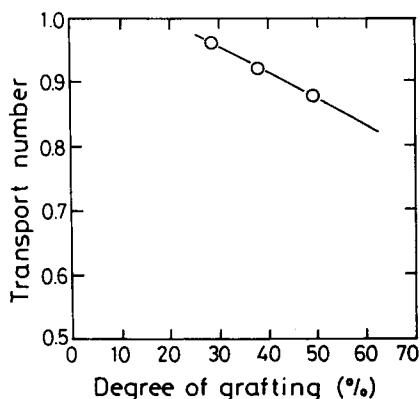


Fig. 7. Transport number vs. degree of grafting. The transport number was measured in 0.5*N* KCl/1.0*N* KCl soln at 20°C. Grafting conditions are the same as in Figure 1.

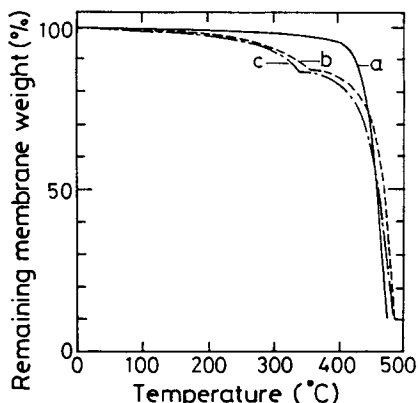


Fig. 8. Thermal decomposition of the grafted membrane: (a) LDPE film; (b) grafted membrane (28.4%); (c) grafted membrane (49.1%). TGA: heating rate, 10°C/min, atmosphere, nitrogen.

Thermal Stability

Figure 8 shows the degree of remaining membrane weight as a function of temperature. The LDPE film used for the grafting substrate starts to decompose at approximately 400°C. The grafted membrane weight begins to decrease at over 100°C, which seems to be caused by dehydration from the membrane. Moreover, grafted membranes have two decomposition starting points at about 300 and 400°C. The second is in accord with that of the LDPE; therefore, the first one is supposed to be caused by grafting chain and/or the substrate decomposition.

Chemical Stability

To investigate oxidation resistance of the grafted membrane the membranes having various grafting percentages were immersed in 3% H₂O₂ solution in the presence of 4 ppm Fe²⁺ at 70°C for 5 h.

Figure 9 shows the degree of weight loss as a function of grafting percentage. The weight loss was negligible at less than 25% grafting. On the other

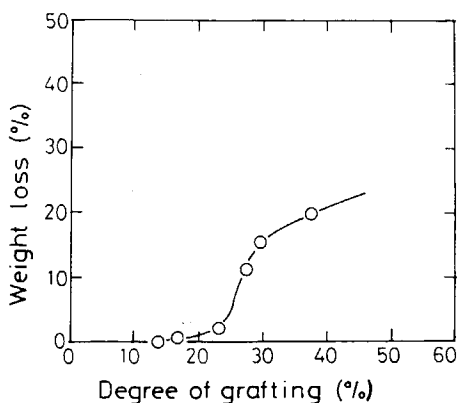


Fig. 9. The chemical stability of the grafted membrane. The grafted membranes were dipped in 3% H_2O_2 soln (Fe^{2+} 4 ppm) at 70°C for 5 h. Grafting conditions are the same as in Figure 1.

hand, the weight loss increased as the grafting percentage increased at more than 25% grafting. As discussed before, at a lower grafting percentage only small amounts of water were absorbed. This means that the oxidizing agent uptake in the grafted membrane was negligible; therefore, the weight loss was very little at a lower grafting percentage.

The weight loss of Nafion 120, a typical perfluoro cation-exchange membrane, was 0.5% under the same oxidizing conditions. Therefore, the grafted membranes are liable to be subject to oxidative degradation compared with perfluoro cation-exchange membranes. One of the main causes is supposed that grafted membranes have LDPE substrate which is subject to oxidative degradation. We will discuss improvements in the grafted membrane oxidative resistance in a future investigation.

CONCLUSION

Investigations of the properties of grafted membranes such as distribution of grafted chains, swelling behavior, electric resistance, transport number, thermal and chemical stability were made. It can be concluded that:

1. Infrared spectroscopy analysis of grafted membranes confirmed the existence of potassium sulfate groups in grafted membranes.
2. Distribution of potassium sulfate groups after the hydrolysis was observed by X-ray microanalyzer, confirming that potassium sulfate groups are located on both surfaces of film at low grafting percentage, and reach the center at more than 25% grafting.
3. Both electric resistance and transport number of the grafted membranes are largely dependent on grafting percentage. Grafted membranes have the possibility of practical use as cation exchange membranes at more than 25% grafting when a homogeneous distribution of ion-exchange groups is established.
4. Grafted membranes have two decomposition starting points about 300 and 400°C .
5. Grafted membranes are liable to be subject to oxidative degradation compared to Nafion 120. Further improvement is needed to achieve high oxidation-resistance membranes.

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