Study on Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. II. Properties of Membrane Obtained by Preirradiation Grafting onto Poly(tetrafluoroethylene)

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Synopsis

Some properties of the membranes obtained by the preirradiation grafting of acrylic acid onto poly(tetrafluoroethylene) (PTFE) film have been studied. The dimensional change by grafting and swelling, water uptake, electric conductivity, and mechanical properties of the grafted PTFE films were measured and were found to increase as the grafting proceeds. These properties were found to be dependent mainly on the degree of grafting regardless of grafting conditions except higher monomer concentration (80 wt %). The electric conductivity and mechanical properties of the membranes at 80 wt % monomer concentration is lower than those at a lower monomer concentration. The results suggest that the membranes obtained at 80-wt % acrylic acid solution have a somewhat heterogeneous distribution of electrolyte groups as compared with those prepared at a monomer concentration less than 60 wt %. X-ray microscopy of the grafted films revealed that the grafting begins at the part close to the film surface and proceeds into the center with progressive diffusion of monomer to give finally the homogeneous distribution of electrolyte groups. The membranes show good electrochemical and mechanical properties which make them acceptable for the practical uses as cation exchange membrane.

INTRODUCTION

Interest in synthetic membranes and membrane processes is rapidly growing. For the last two decades, membranes have been increasingly introduced as an effective and economical means for the separation of molecular mixtures. Today, their applications range from desalination of saline waters and artificial kidneys and lungs to separation and fractionation of gases or micromolecular mixtures.

Fluorine-containing polymers have drawn much attention in the past and gained wide practical use because of their excellent thermal, chemical stability, and mechanical properties. The grafting of hydrophilic monomers onto poly(tetrafluoroethylene) (PTFE) films have been studied by various methods.[1–6] Very recently Chapiro and Jendrychowska-Bonamour[1] studied the grafting of various monomers such as styrene, acrylic acid, and 4-vinylpyridine onto PTFE films by using the direct grafting method. They found that the common feature of the grafted PTFE films is the fairly homogeneous distribution of the active

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sites throughout the bulk of the film and their outstanding mechanical strength even in the swollen state. Munari et al.[2] investigated the properties of the PTFE–*g*-styrene membranes obtained by preirradiation method. They found that the sulfonated membranes show mechanical properties similar to PTFE film that has undergone the same process of grafting and good electrochemical behavior. Jendrychowska-Bonamour and Millequant[3] studying the direct grafting of *N*-vinylpyrrolidone onto PTFE to find that the transfer of both ions and water is a function of the free volume in the films, it depends on the grafting ratio and is not influenced by the preparation conditions.

We have studied the kinetics of radiation-induced grafting of acrylic acid onto PTFE films by the preirradiation method reported previously.[7] In the present study, the electrochemical, mechanical, and swelling properties and grafting distribution of the grafted PTFE films have been investigated. The purpose of this study is to give support for the grafting mechanism proposed in the previous study and also to show a possibility for the practical application of the grafted membrane as an ion-exchange membrane.

EXPERIMENTAL

Materials

The grafted PTFE films were obtained by the preirradiation grafting. The materials, such as monomer (acrylic acid) (AAC) and polymer substrate (PTFE), and the grafting procedure were described in detail in the previous study.[7] The other chemicals were reagent grade and used without further purification.

Swelling Behavior

The grafted PTFE films with a known weights were immersed in distilled water at room temperature (25°C) until equilibrium have been reached (24 h in most cases). Then the films were taken out and the excess water attached on the surface was quickly removed by a blotting paper and weighed. 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 films, respectively.

Dimensional changes of the membranes, caused by swelling, were also determined by measuring the dimensions of the samples before and after swelling. The film thickness was measured by using a thickness gauge (Ono Sokki, TG-601).

Electric Resistance

The grafted films were treated with 2.5% KOH solution for 24 h at 100°C to convert the carboxylic acid groups into potassium salt. The grafted membranes, thus obtained, were conditioned by immersing in 3*N* KCl solution for 48 h at 100°C. The electric resistance was measured in 3*N* KCl solution at 20°C using an ohmmeter (LCR Meter 4261, Yokogawa-Hewlett-Packard) working at 1000 Hz.

Grafting Distribution

The grafting distribution in the polymer matrix was investigated by X-ray microanalyzer (JXA-Superprove 773, Japan Electron Optics Laboratory Co., Ltd.). The grafted film, pretreated with 2.5% KOH solution, was cut perpendicularily to its surface at liquid nitrogen temperature, and its cross section was observed.

Transport Number

The grafted film with potassium form was conditioned by being kept in 0.5N KCl solution for 5 min at 100°C and overnight at 20°C and then placed in between two compartments and ion electrodes to measure the electromotive force of chemical cell. 0.5 and 1.0N KCl solutions were made to flow individually through the compartments until equilibrium has been reached, and the potential was measured at 20°C using an ion meter (Micro-Processor Ionanalyzer 1901 Orion Research). Transport number ($\bar{t}$) of counter ions in the membrane was calculated from the value of the measured potential (E_m) by using the following equation:

$$\bar{t} = E_m/2\,E_0 + 0.5$$

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

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

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

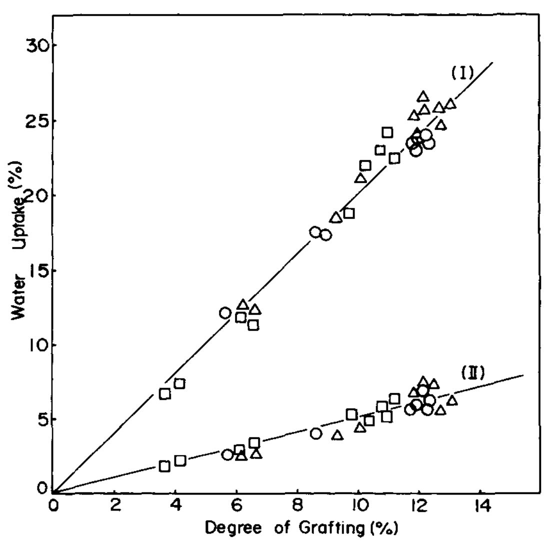


Fig. 1. Water uptake vs. degree of grafting for the grafted PTFE films obtained at various preirradiation doses. Swelling temp = 25°C; grafting conditions: acrylic acid conc = 40 wt %; grafting temp = 35°C; original film thickness = 80 μm. Doses (Mrad): (□) 1; (○) 5; (△) 10.

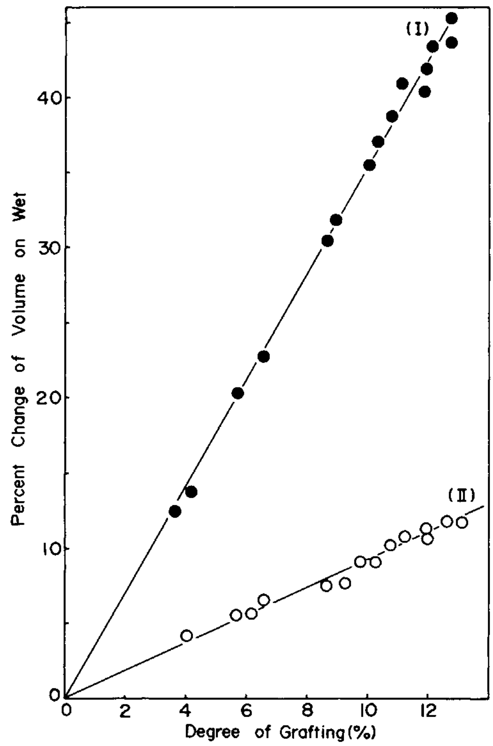


Fig. 2. Percent change of volume on wetting as a function of degree of grafting. Swelling temp = 25°C; grafting conditions, except preirradiation dose (5 Mrad), are the same as in Figure 1.

Mechanical Properties

Dumbell-shaped samples with dimensions of 63 mm length, a neck length of 25 mm, and 3 mm width were used. The measurements were carried out by using an Instron (Model 1130, Corp., Canton, Mass.) and crosshead speed 5 cm/min.

RESULTS AND DISCUSSION

Swelling Behavior

Swelling behavior is one of the characteristic properties of the grafted PTFE film due to the presence of hydrophilic groups. In this study, the swelling behavior for the membranes obtained at different grafting conditions was investigated. Figure 1 shows percent water uptake against percent grafting for the membranes obtained at various preirradiation doses. It can be seen that water uptake increases with percent grafting for both membranes, those which were treated with KOH solution and the untreated ones. For the treated membrane, water uptake is enhanced due to the increase of hydrophilicity by converting the carboxylic acid groups into their potassium salt. It is obvious that the preirradiation dose has no influence on the water uptake of the films.

Figure 2 shows the extent of swelling expressed as the percentage increase in volume ($\Delta V\%$) as a function of percent grafting. The difference between the swelling behavior of the KOH-treated membranes (I) and the untreated ones

(II) was considerable in the whole grafting range; the treated one possesses higher swelling. The treated membrane became much more smooth and flat as compared to the untreated one.

It was also observed that the grafting conditions, such as temperature, preirradiation dose, and film thickness have no effect on the swelling properties of the grafted films which is in agreement with that obtained for water uptake shown in Figure 1.

It can be suggested that the swelling behavior of the grafted PTFE films depends mainly on the degree of grafting and is independent of the preparation conditions.

Electric Resistance

Figure 3 shows the relationship between specific electric resistance and the percent grafting for the membranes obtained at various preirradiation doses. It is obvious that the electric resistance decreases as the percent grafting increases, and falls down rapidly in the range of 7–9% grafting. At these experimental conditions, the specific electric resistance depends mainly on the amount and distribution of the electrolytes in the grafted films, and is independent of the preirradiation dose. These results can be reasonably understood by assuming

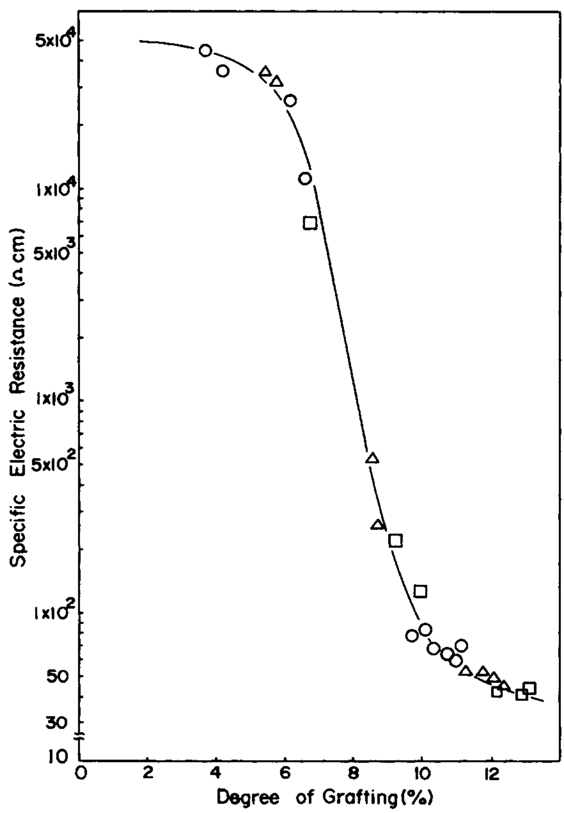


Fig. 3. Logarithmic plots of the specific electric resistance vs. degree of grafting for the grafted PTFE films obtained at various preirradiation doses. Grafting conditions are the same as in Figure 1. Doses (Mrad): (△) 1; (○) 5; (□) 10.

that the grafting proceeds from the surface to the center of the film with progressive diffusion of monomer. In the region where the membrane has a higher electric resistance, the grafting does not proceed into the center of film. The abrupt fall in the electric resistance of the membrane at a percent grafting of 7–9% indicates that the grafting front reaches the center of film at a percent grafting more than 9%.

The effect of monomer concentration on the electric resistance of the grafted films was investigated and shown in Figure 4. The results show that the electric resistance decreases with increasing the percent grafting and is independent of the monomer concentration ranging from 10% to 60% and that it depends mainly on the percent grafting. At higher monomer concentration (80%), however, the abrupt fall in the electric resistance was found to deviate to a higher percent grafting (around 12%). This suggests that the graft polymerization at 80% acrylic acid solution is heterogeneous and occurred in the part close to the film surface until the degree of grafting goes up to over 12%, and therefore the electric resistance decreased rapidly at 16% grafting, at which the grafting proceeds completely through the film.

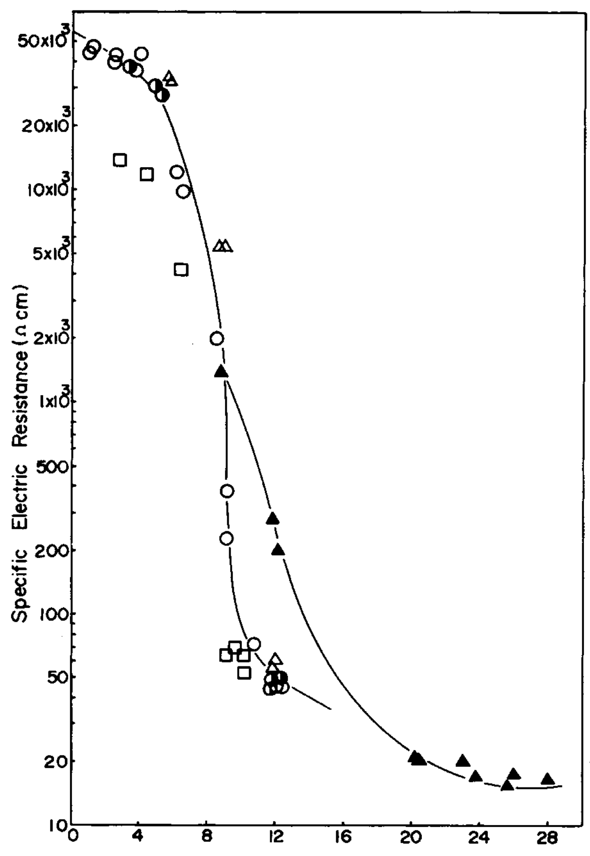
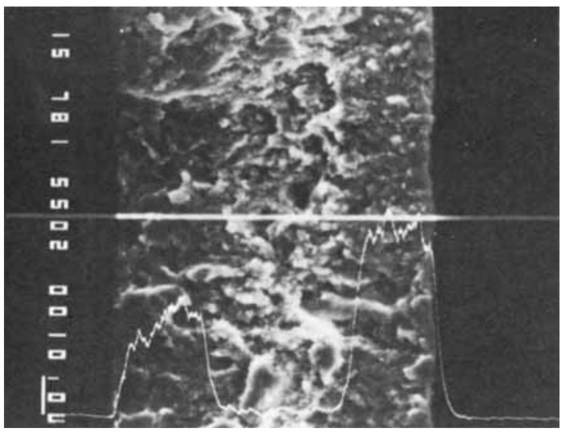


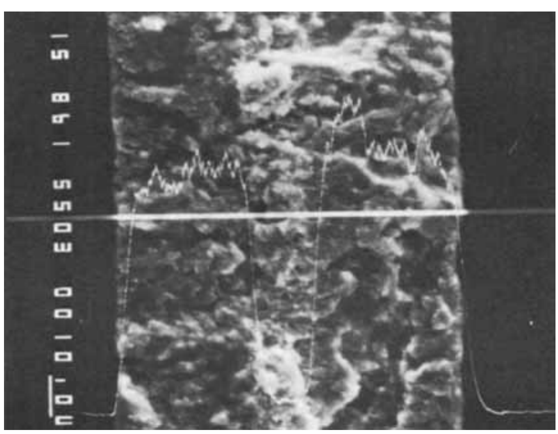
Fig. 4. Logarithmic plots of the specific electric resistance vs. degree of grafting for the grafted PTFE films obtained at various acrylic acid concentrations. Grafting conditions, except preirradiation dose (5 Mrad), are the same as in Figure 1. AAc concentrations (wt %): (○) 10; (◑) 20; (△) 40; (□) 60; (▲) 80.

Grafting Distribution

In order to confirm the grafting mechanism discussed above and to elucidate the grafting distribution in the direction of film thickness, cross section of the membrane was observed by X-ray microanalyzer. Figure 5 shows the change in the grafted layer for membranes obtained at a constant monomer concentration (40%). The grafting proceeds from both surfaces of the film into the center part. At a lower degree of grafting less than 9% [Figs. 5(a) and 5(b)], the nongrafted layer still remains in the middle part of film, and then disappears, as the grafting proceeds, to give a membrane with a homogeneous distribution of grafted chains [Fig. 5(c)]. Figure 6(a) shows a membrane with 12.2% grafting, prepared at 80% monomer concentration; it still has the nongrafted layer in spite of its higher degree of grafting as compared to that obtained at 40% monomer

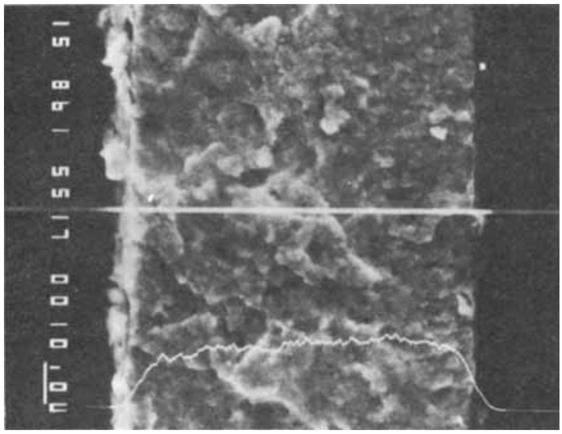


(a)



(b)

Fig. 5. XMA micrograph of the grafted PTFE film. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid conc = 40 wt %; original film thickness = 80 μm; grafting temp = 35°C. (a) Degree of grafting = 5.8%; specific electric resistance = 3.4×10^4 Ω·cm; K_α intensity, $\times$ 1. (b) Degree of grafting = 9.0%; specific electric resistance = 5.5×10^2 Ω·cm; K_α intensity, $\times$ 1. (c) Degree of grafting = 11.9%; specific electric resistance = 62.0 Ω·cm; K_α intensity, $\times$ 1/5.



(c)

Fig. 5. (*Continued from previous page.*)

concentration. The nongrafted layer disappeared completely at higher degree of grafting [Fig. 6(b)].

The thickness of the grafted layer in the membranes was calculated from XMA photographs and plotted as a function of grafting degree (Fig. 7). It can be seen that, at the same degree of grafting, the thickness of the grafted layer is independent of the preirradiation dose, and depends mainly on the degree of grafting. On the other hand, the dimensional changes caused by grafting were measured for the dry membranes obtained at two different monomer concentrations (40% and 80%) and are shown in Figures 8 and 9. It can be seen that, for both membranes, the film thickness increases as the grafting begins. The rates of increase in film thickness tend to decrease above 5% and 12% grafting for the membranes obtained at 40% and 80% acrylic acid concentrations, respectively. It was also found that changes in width and length have an induction period which is longer at 80% monomer concentration. The increases in width and length of film begin at almost the same range of grafting at which the rate of increase in thickness decreases.

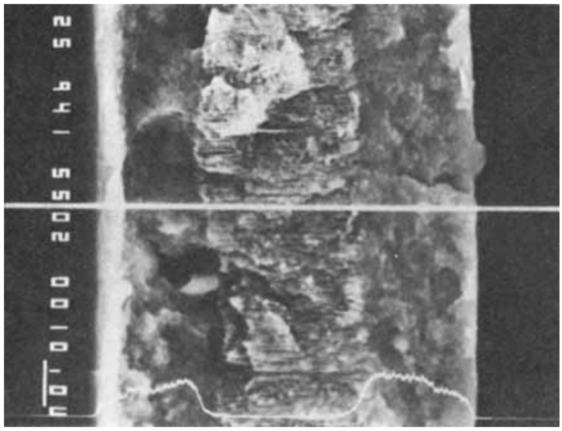
From this result, it is supposed that, at a lower degree of grafting, the nongrafted layer prevents dimensional changes in directions of length and width but not in thickness of the film.

The results of grafting distribution and dimensional change suggest that the lower the monomer concentration, the more deeply the grafting proceeds at the same percent of grafting, i.e., the distribution of grafting is more homogeneous at a lower monomer concentration.

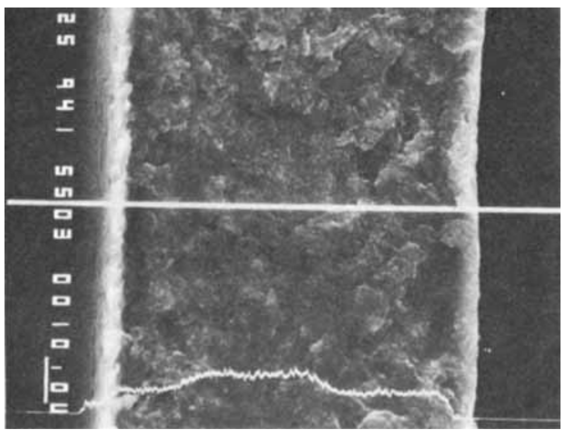
Transport Number

The permselectivity of membrane is one of the most important properties for ion exchange membrane. The transport number of counter ions in the grafted PTFE films were measured.

Table I shows the transport number of the membranes obtained at various preirradiation doses. It can be seen that the transport number is not influenced by the preirradiation dose. It can be assumed that these membranes are useful as cation exchange membranes.



(a)



(b)

Fig. 6. XMA micrograph of the grafted PTFE film. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid conc = 80 wt %; original film thickness = 80 μm; grafting temp = 35°C. (a) Degree of grafting = 12.2%; specific electric resistance = 199.0 Ω·cm; K_α intensity, × 1/50. (b) Degree of grafting = 25.6%; specific electric resistance = 15.6 Ω·cm; K_α intensity, × 1/50.

Mechanical Properties

It is well known that PTFE is very sensitive for ionizing radiation, and shows significant damage at exposures as low as 0.04 Mrad.[8] Figure 10 shows the changes of tensile strength (T_b) and percent elongation (E_b) at break point of the ungrafted PTFE film which was irradiated under vacuum at room temperature. It can be seen that both T_b and E_b are remarkably decreased upon irradiation. It is important that the grafted film have an acceptable mechanical properties for handling in the practical use. The changes of T_b and E_b for the grafted PTFE film obtained at various preirradiation doses were measured as a function of percent grafting and shown in Figure 11. From the practical point of view, as the membranes will be used on wetting, it is reasonable to measure T_b and E_b after the films are soaked in distilled water for 24 h. The results show that the grafted PTFE gave good mechanical properties which make them ac-

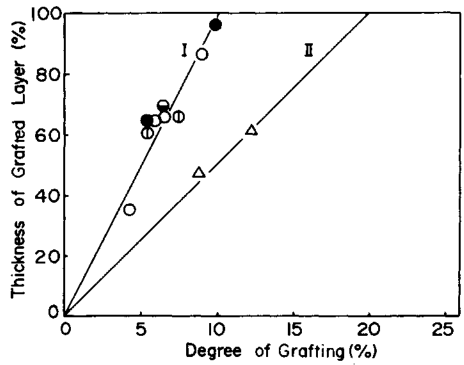


Fig. 7. Percent thickness of the grafted layer vs. degree of grafting for the membranes obtained at various preirradiation doses and monomer concentrations: (I) 40 wt % AAc; (II) 80 wt % AAc. Doses (Mrad): (●) 1; (◐) 3; (○) 5; (◒) 10.

ceptable for practical uses, although T_b and E_b decreased with increasing preirradiation dose.

Also, the changes of T_b and E_b of the grafted PTFE films, obtained at various monomer concentrations, were measured as a function of percent grafting, shown in Figure 12. It can be seen that, for lower monomer concentrations, E_b slightly increase with percent grafting, but T_b has no significant change. For higher monomer concentration (80%), however, both T_b and E_b decrease sharply at a lower percent grafting and increase gradually again with increasing percent grafting. As discussed above, the grafting with higher monomer concentrations proceeds rapidly at the part close to the film surface, especially, at a lower degree of grafting. Therefore, the heterogeneity of grafting may cause some stresses on the polymer matrix to decrease their mechanical properties. Also, it expected

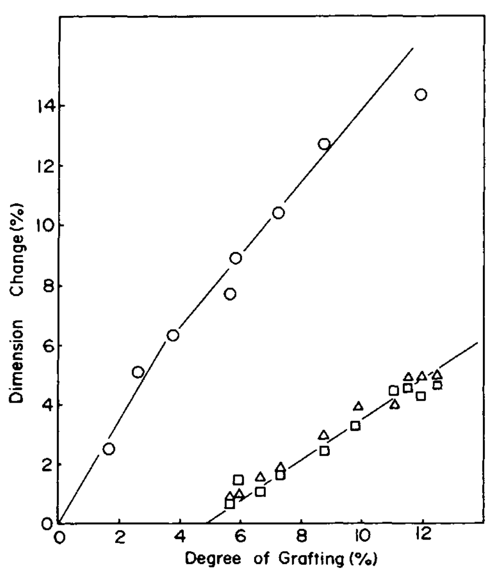


Fig. 8. Dimensional changes of the grafted PTFE films on dry state as a function of degree of grafting. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid concentration = 40 wt %; grafting temp = 35°C; original film thickness = 80 μm. (○) Thickness; (△) width; (□) length.

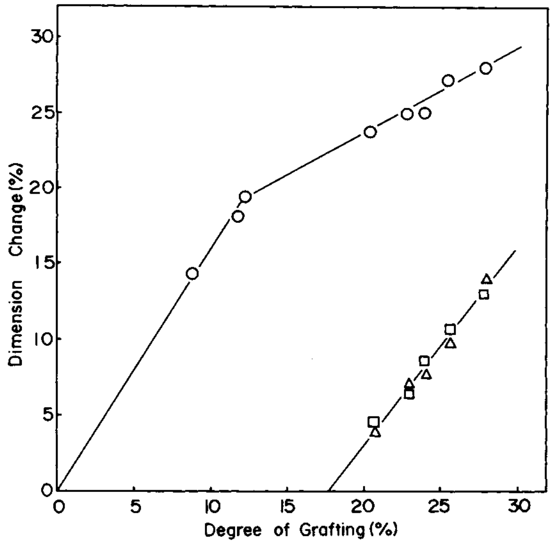


Fig. 9. Dimensional changes of the grafted PTFE films on dry state as a function of degree of grafting. Grafting conditions, except acrylic acid concentration (80 wt %), are the same as in Figure 6. (○) Thickness; (△) width; (□) length.

that such stress may be enhanced on wetting due to the hydrophilicity of grafted chains. At a higher degree of grafting, however, such stress may disappear, as the grafting proceeds thoroughly in the polymer matrix.

These results indicate that the mechanical properties of the grafted PTFE film are affected largely by the grafting distribution as well as preirradiation dose.

CONCLUSION

Investigation of the properties of the grafted PTFE, which was prepared by the preirradiation method, show the possibility of its practical use as cation exchange membrane. By converting the carboxylic acid groups into potassium salt, the grafted films become much smoother and flatter and have a higher water uptake and swelling behavior. The electric resistance of the grafted films decreases as the percent grafting increases. It was also found that the electric resistance and grafting distribution have some dependency on monomer concentration higher than 60%, and that they are independent of preirradiation dose.

TABLE I
Transport Number of Membrane at Various Preirradiation Doses

Sample no.	Preirradiation dose (Mrad)	Degree of grafting (%)	E_m (mV)	Transport number (t)	Specific electric resistance (Ω·cm)
1	1	11.2	11.8	0.88	71.4
2	3	11.9	11.8	0.88	62.4
3	5	12.4	12.1	0.89	49.0
4	10	13.1	11.8	0.88	46.2

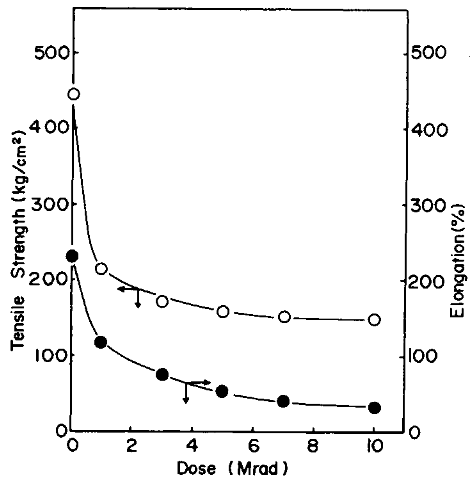


Fig. 10. The change of mechanical properties of the original PTFE films caused by γ-rays irradiation in vacuo at room temperature.

The homogeneity of grafting distribution at lower monomer concentrations (10–60%) is much more than that at higher ones (80%). Although the grafted PTFE films show mechanical properties similar to that of PTFE matrix, which depends largely on the preirradiation dose, it is acceptable for the practical applications when it has the homogeneous distribution of grafting.

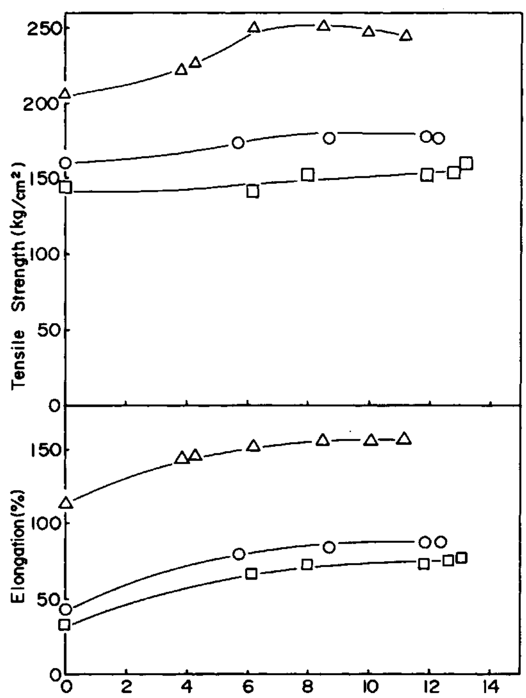


Fig. 11. The change of mechanical properties of the grafted PTFE films on wetting as a function of degree of grafting. Grafting conditions are the same as in Figure 1. Doses (Mrad): (△) 1; (○) 5; (□) 10.

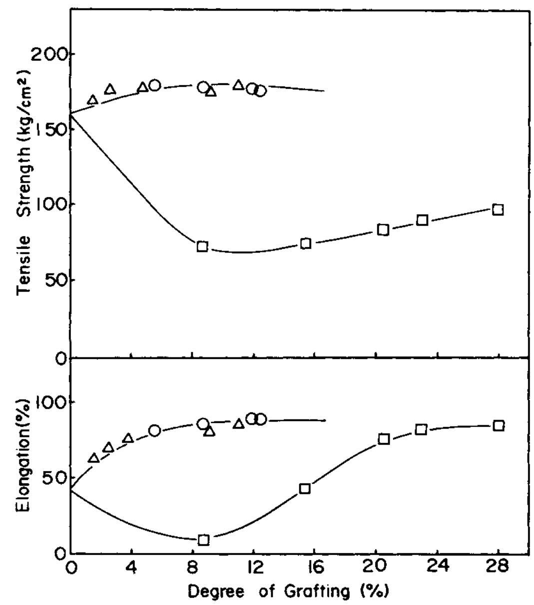


Fig. 12. The change of mechanical properties of the grafted PTFE films on wetting as a function of degree of grafting. Grafting conditions, except acrylic acid concentration (80 wt %), are the same as in Figure 6. AAc concentrations (wt %): (△) 10; (○) 40; (□) 80.

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