

# Electrical and Other Properties of Mutual Radiation-Induced Methacrylic Acid Grafted Polyethylene Films

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## Synopsis

The radiation-induced grafting of methacrylic acid onto polyethylene films was applied to the synthesis of ion-exchange membranes. The grafting yield increased at first then decreased with the increase in the irradiation dose. The surface area, thickness, volume, and the water uptake of the grafted film increased linearly with the increase in grafting yield. The distribution pattern of carboxyl groups of graft chains in the direction of film thickness followed by EPMA line profiles of potassium which combined with carboxyl groups showed that a homogeneous distribution was not obtained until the grafting yield was more than 10%. When DC current was supplied to the membrane in NaOH solution, the reciprocal of the electric resistance increased with the increase in NaOH concentration. The specific electric resistance decreased exponentially with the increase in the content of ionic functional groups in the membrane. The steady state concentration of Na<sup>+</sup> in catholyte and the current efficiency were ca. 15 and 20%, respectively.

## INTRODUCTION

Many attempts have been made to produce ion-exchange membranes by the radiation-induced graft copolymerization of acid monomers like acrylic acid and methacrylic acid onto commercially available polymer films.<sup>1-10</sup> The utilization of radiation grafting has several advantages: (i) the wide selectivity of trunk polymer films for membranes, (ii) the extensive possibilities of introducing monomers of different functional groups, and (iii) a considerable controllability of the amount and the distribution of functional groups in the membrane.

In spite of many works until now, however, the relationship between the grafting conditions and the physical and chemical properties of such membranes is still not clear. These properties change according to the combination of trunk polymers/monomers and the reaction conditions such as irradiation dose, dose rate, temperature, concentration of monomer, etc. In addition, the absolute values of these properties depend on the method of measurement. Therefore, an accumulation of data in this field may be necessary for establishing the reaction conditions for the synthesis of the desired ion-exchange membranes by radiation-induced grafting.

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In the present study, we chose the polyethylene-methacrylic acid system and studied grafting features, physical and chemical changes of the grafted films, and electrical properties.

### EXPERIMENTAL

A low density polyethylene (PE) film (Ziploc-Dow Chemical) of thickness 0.025 mm was cleansed with acetone and dried in a vacuum oven overnight before use. Both methacrylic acid (MAc) and acrylic acid (AAc) from Eastman were purified by a usual distillation. Solvents (benzene, methanol) were used as supplied.

The films of size  $4 \times 4$  cm and 20 mL of monomer solution were introduced into a glass ampoule, which was evacuated by repeating freeze-thaw cycles at least three times before seal under vacuum (ca.  $1 \times 10^{-4}$  Torr). The reaction was carried out in a cobalt-60 gamma ray source at a dose rate of  $0.2 \times 10^6$  rad/h. The homopolymer and the unreacted monomer were extracted by boiling the irradiated mixture with 1 L of water overnight with the water being exchanged with fresh water. This procedure was repeated three times. The grafting yield was obtained from the weight increase of the film. The water uptake with the grafted film was measured as follows: The sample film was preliminarily immersed in water for 24 h at room temperature. Then, the surface of the film was quickly wiped with filter papers, and the weight change was followed by the microbalance at room temperature. The water uptake was obtained as the percent weight increase from the dried sample.

The distribution of graft chains inside the film in the direction of thickness was obtained with a JEOL electron-probe X-ray microanalyzer (Model JXA-733). The sample film was preliminarily boiled in 2.5 wt % KOH solution overnight, followed by immersing in fresh water for 2 days. The K-alpha X-ray from potassium, which was combined with carboxyl groups of graft chains was detected and its line profile in the cross section of the film was measured as shown in detail in our previous papers.<sup>7-10</sup>

For the measurement of electrical properties of the grafted films, the apparatus as shown in Figure 1 was used. The volume of each cell was 110 cm<sup>3</sup>. The grafted film, which was preliminarily boiled in NaOH solution, was installed between the two cells containing NaOH solution of the same concentration. The DC current was supplied by a Keithley current source (Model 225), and the voltage drop between the two cells was followed by a Keithley electrometer (Model 602). The electrodes for the current source were #6 stainless steel mesh (cathode) and perforated (2 mm $\phi$ ) nickel plate (anode), and those for the electrometer were platinum wires (20 gauge). The electric resistance of films was measured without circulating the NaOH solution, while the current efficiency and steady state concentration were obtained by circulating the solution between the anode cell and a NaOH reservoir (2 L). The resistance  $R$  was calculated by the next equations:

$$V = V_m - V_0 \quad (1)$$

$$R = V/I \quad (2)$$

where  $V$ ,  $V_m$ ,  $V_0$ , and  $I$  indicate net voltage drop, voltage with membrane,

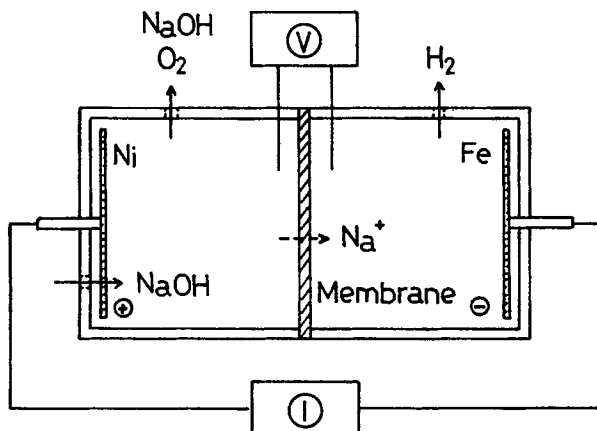


Fig. 1. The apparatus for the measurement of electric resistance of membranes, steady state concentration of catholyte, and current efficiency. I and V denote the current source and electrometer, respectively.

that without membrane, and the supplied electric current, respectively. The current efficiency was calculated by the ratio of the amount of NaOH obtained to the theoretical amount of NaOH based on the supplied current for a prescribed period.

## RESULTS AND DISCUSSION

### Grafting

Figure 2 shows a comparison of the grafting yield of MAc onto PE films and that of AAc at various irradiation doses up to 5 Mrad. In the case of AAc, the initial rapid increase in the grafting yield (90%/h) was followed by a slow increase (2%/h). The rapid increase is probably due to the evolution of heat in the glass ampoule because the ampoule was not heat-controlled during the irradiation. The accumulation of the heat of polymerization and of the heat due to the irradiation can accelerate the reaction in the initial stage. The following slow increase may be due to the slow step of the supply of hydrophilic AAc to the hydrophobic trunk polymer after consuming the preliminarily absorbed AAc. The diffusion of monomer in the polymer is sometimes the rate-determining step when the grafting is carried out by the mutual irradiation method.<sup>11</sup> On the other hand, in the case of MAc, the increase in the grafting yield in the initial stage was much slower and even a decrease was observed after 1 Mrad irradiation. The decrease indicates the possibility of the radiation-induced degradation of growing graft chains of poly(methacrylic acid) because the degradation of PE trunk polymer is not marked under the present irradiation condition. Poly(methacrylic acid) is known as a radiation-degradable polymer.<sup>12</sup> A similar degradation of graft chains during the irradiation has been reported in the case of grafting methacrylic ester.<sup>13</sup>

The change in the grafting yield of MAc is affected by the presence of solvents. Figure 3 shows the effect of solvents on the grafting yield of MAc.

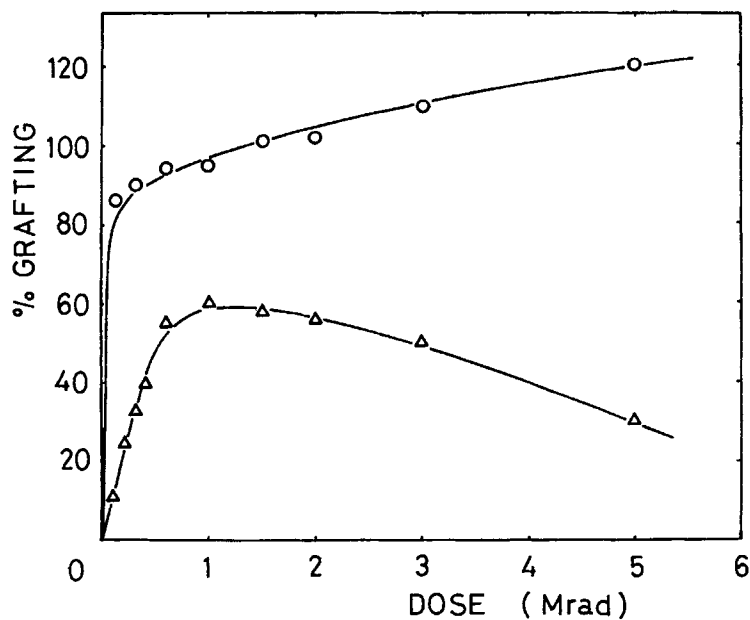


Fig. 2. Comparison of grafting yield of MAc onto PE films and that of AAc at various irradiation doses: ( $\Delta$ ) MAc, ( $\circ$ ) AAc.

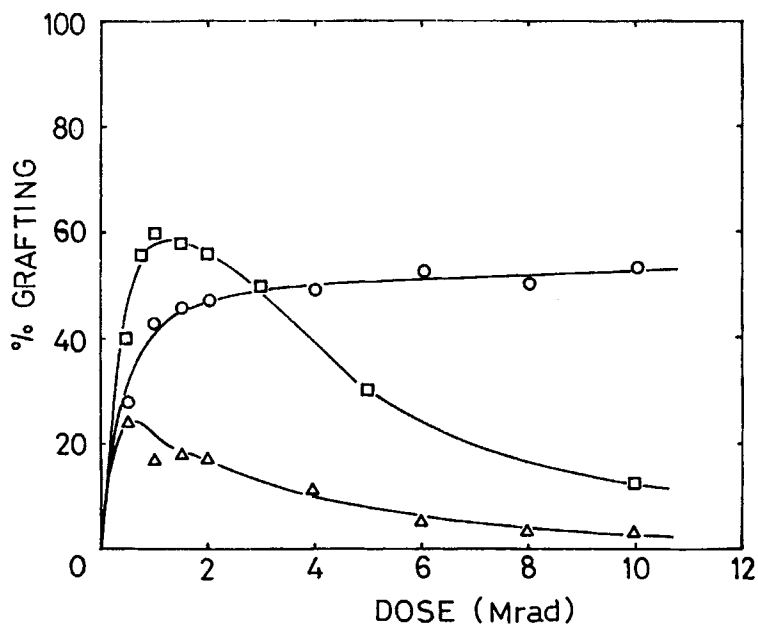


Fig. 3. Effect of solvent on the grafting yield of MAc: ( $\square$ ) neat MAc, ( $\circ$ ) in benzene, ( $\Delta$ ) in methanol. The concentration of MAc is 50 vol-%.

The concentration of MAC in each solvent is 50 vol %. The change in grafting yield obtained in the presence of methanol is similar to the change obtained with neat MAC. The highest grafting yield, however, is less than half that of neat MAC and the maximum appears earlier. In the presence of benzene, on the other hand, the grafting yield increases, followed by leveling off. This change is quite similar to the change observed with AAc as shown in Figure 2. Because poly(acrylic acid) is a radiation-crosslinkable polymer,<sup>12</sup> the similarity of the grafting feature of PE-MAC in the presence of benzene to that of PE-AAc indicates that the degradation of graft chains of poly(methacrylic acid) is suppressed by the presence of benzene in the reaction site. Presumably, the radiation energy is partly absorbed and consumed as the resonance energy among benzene rings, which reduces the radiation degradation of poly(methacrylic acid) graft chains.

### Physical and Chemical Changes of Films

The grafted film can absorb water according to the grafting yield as shown in Figure 4. The linear increase indicates that the water uptake is due to the hydrophilic acid groups of the graft chains.

Figure 5 shows the changes in dimension of the polymer film with grafting. Although both the thickness and the surface area of the film increase linearly with the increase in the grafting yield, the change in the thickness is almost twice as large as the change in area. These increases are due to the packing of graft chains inside the polymer film. Because the graft polymerization occurs mainly in the amorphous region, the packing of graft chains is thought to expand the amorphous region of the film. The crystalline region, on the other hand, is little affected by grafting.<sup>14</sup> In other words, the grafting and the resultant expansion of the trunk polymer occur mainly at the mechanically weak part of the trunk polymer. In this connection, it is pointed out that the film surface is highly oriented in the direction of extrusion which provides the film surface the toughness to resist against the expansion. The broken line in

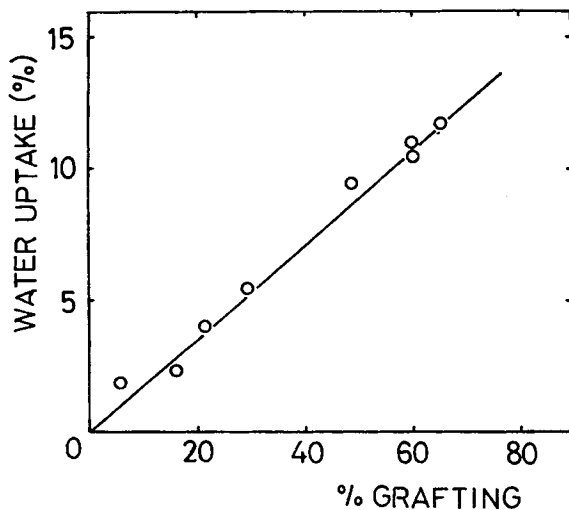


Fig. 4. Water uptake vs. grafting yield.

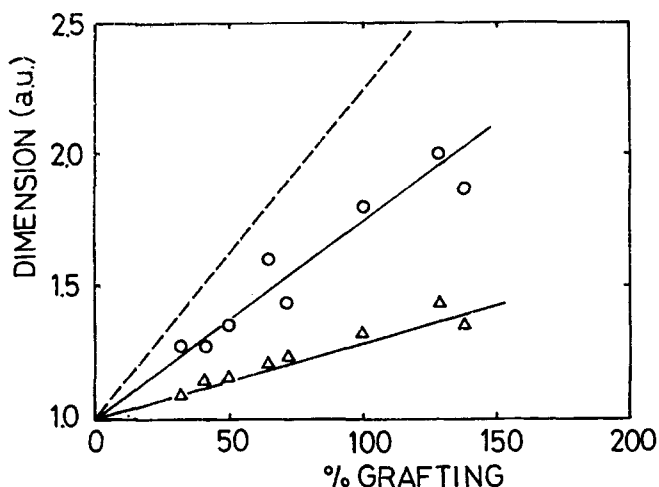


Fig. 5. Changes in dimension of the polymer film with grafting: ( $\Delta$ ) area, ( $\circ$ ) thickness, (---) volume (= area  $\times$  thickness).

Figure 5 shows the volume change of the grafted film, calculated from the thickness and area. The volume is, for example, expanded approximately twice as large as the original volume when the amount of the graft chains is equal to that of the trunk polymer (grafting yield = 100%).

The packing of graft chains inside the film does not always proceed homogeneously in the direction of film thickness.<sup>7-10</sup> In order to clarify the homogeneity of packing, the measurement of EPMA line profiles of potassium which was combined with carboxyl groups of graft chains was carried out. Figure 6 shows the distribution patterns of graft chains obtained at different grafting yields. When the grafting yield is small (in the present case, less than 10%), the grafted chains exist only near the surface regions of the film. With the increase in the grafting yield, the two peaks observed in Figures 6(a) and (b) are enlarged till they make a flat curve as shown in Figures 6(c) and (d). Once a homogeneous distribution curve is obtained, the level of the distribution curve increases with the increase in the grafting yield. The homogeneous distribution in the direction of film thickness is important for the transport of ions when the electric current is supplied to the film as shown in Figure 1. Actually, no ions could pass through the film if there existed a nongrafted layer in the direction of film thickness.

### Electrical Properties

The films of homogeneous distribution of grafted chains in the direction of film thickness were submitted to the measurement of electric resistance with the cell containing NaOH solution. The observed voltage drop between the two cells in the presence of the films  $V_m$  was larger than that without membrane  $V_0$ . The concentration of NaOH solution was changed from 0.9 to 25 wt %. Both  $V (= V_m - V_0)$ , and the resultant electric resistance of the film  $R (= SV/I$ , where  $S$  = surface area of the film and  $I$  = current) changed with the change in the alkaline concentration, as shown in Figure 7. From the slope

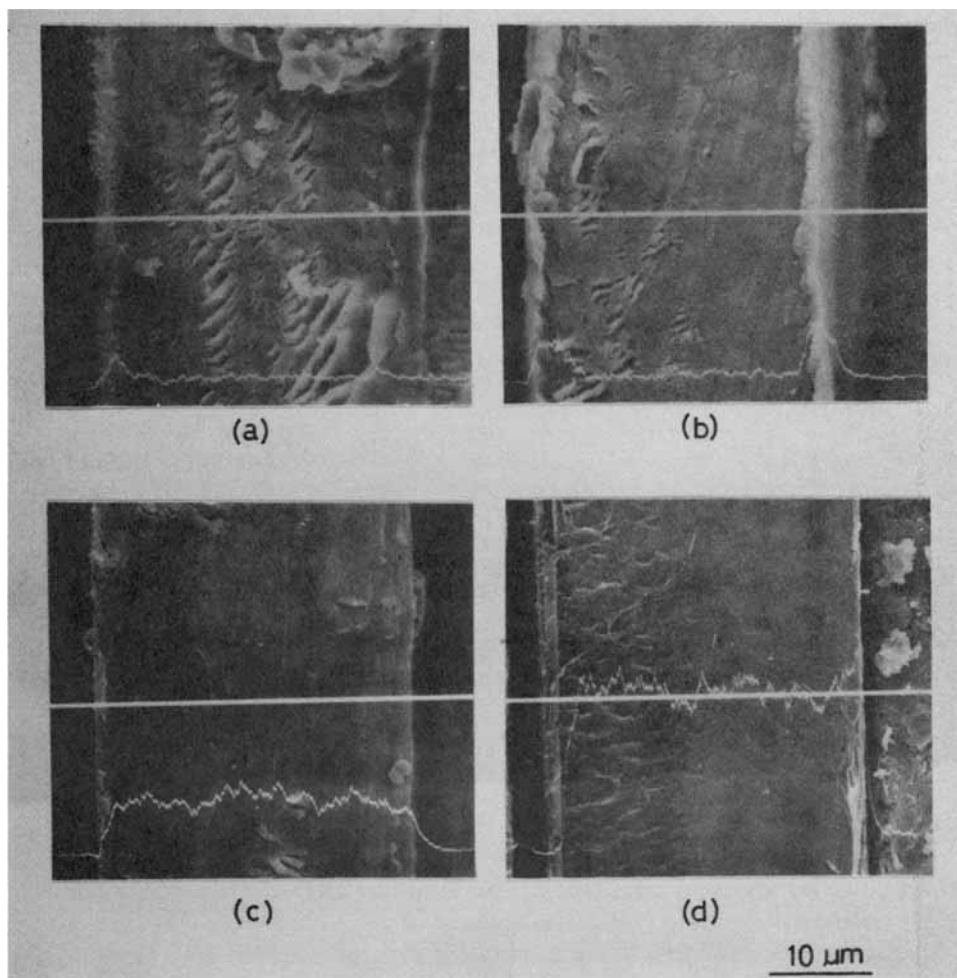


Fig. 6. Distribution pattern of graft chains in the direction of film thickness: (a) % graft = 0.5, (b) 5.8, (c) 33.1, (d) 54.6. The straight lines show the scanned place of the film.

of the straight line in Figure 7, the following relation was obtained:

$$1/R \propto [\text{Na}^+] \quad (3)$$

Because the film was preliminarily conditioned with NaOH solution overnight, the carboxyl groups of graft chains are completely changed to the form  $-\text{COONa}$ . When DC current is supplied,  $\text{Na}^+$  ions in the anode cell go through the film to the cathode cell by passing the fixed counter ion parts. Equation (3) indicates that the reciprocal of  $R$  (or the conductivity) of the film is proportional to the concentration of  $\text{Na}^+$  ions in the solution. In other words, the transport of  $\text{Na}^+$  ions depends on the first order of the concentration gradient of  $\text{Na}^+$  ions between the two cells.

Because the electric resistance of the film depends on the film thickness which increases with the grafting yield, normalization of the resistance value is necessary in order to compare the resistance among the films of different

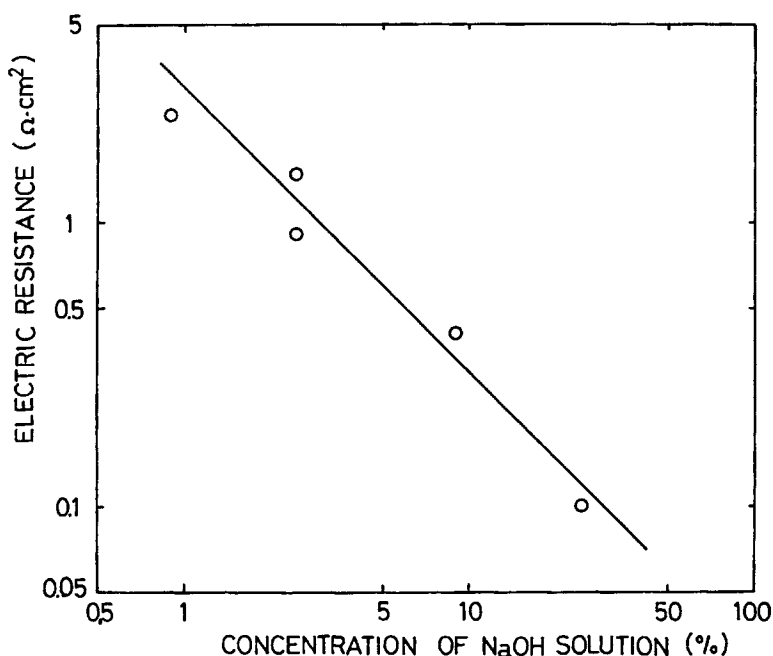


Fig. 7. Electric resistance of the films vs. concentration of NaOH solution in the cells.

grafting yields. Figure 8 shows the relationship of the specific resistance  $R'$  ( $= R/L$ ,  $L$  = thickness) at the NaOH concentration of 12.3 wt % and the weight fraction of graft chains  $G/100 + G$  ( $G$  = % grafting). The straight line obtained by the semilogarithmic plot indicates that the specific resistance decreases exponentially when the amount of graft chains (functional groups) increases. The empirical formula shown in Figure 8 is given as

$$R' \propto \exp[-11.2(G/100 + G)] \quad (4)$$

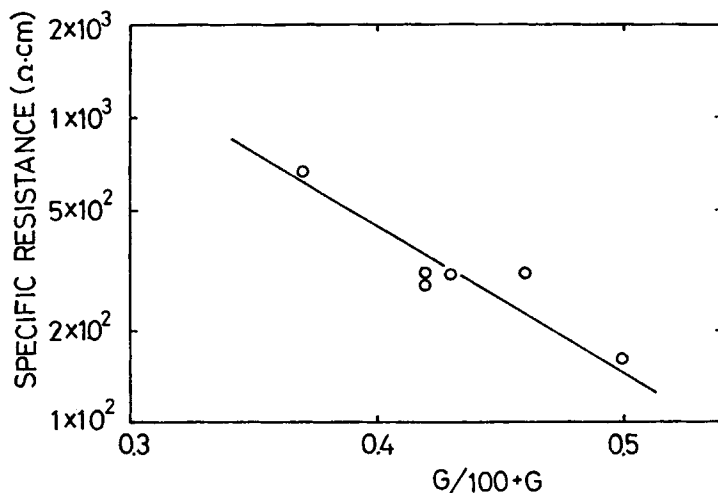


Fig. 8. Specific resistance vs. weight fraction of graft chains  $G/100 + G$  ( $G$  = % graft).



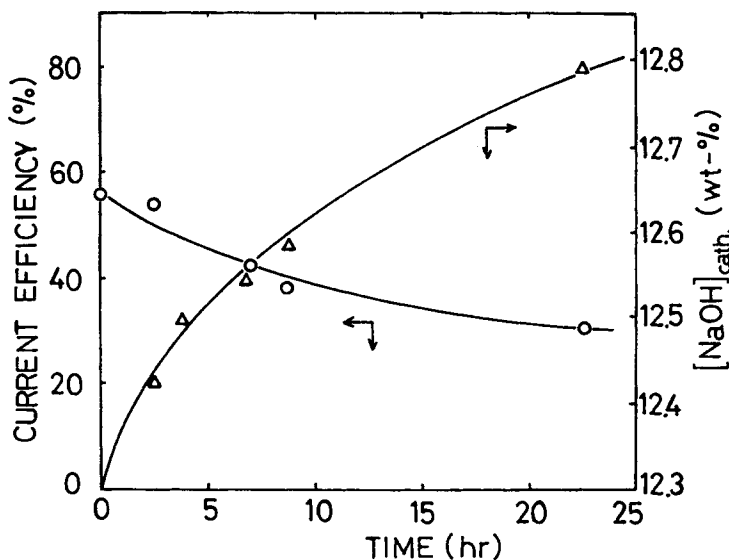


Fig. 9. Changes in the steady state concentration of  $\text{Na}^+$  in catholyte and the current efficiency with time: ( $\Delta$ ) steady state concentration; ( $\circ$ ) current efficiency.

The large index in the exponential term 11.2 indicates that the specific resistance is sensitive to the change in the amount of grafted chains inside the film. This result is based on the distribution of graft chains in the film. The polyelectrolyte graft chains may assemble to make ionic clusters. The increase in the amount of graft chains brings about the network formation of these clusters, which is important as a route for the transport of ionic species through membranes.<sup>15</sup> The above-mentioned sensitive change in specific resistance is thought to be related to this network formation. That is, just a little increase in the amount of network formation is a breakthrough for decreasing the specific resistance of the membrane.

In order that the grafted film is applied to the chlor-alkali cell, the film must possess a high current efficiency and a sufficient steady state concentration of solution during the operation under the supply of electricity. The grafted films were mounted in the cell containing NaOH solution of 12.3% as shown in Figure 1 and the DC current was supplied continuously. With the progress of electrolysis, the concentration of  $\text{Na}^+$  ions in the catholyte increased from the initial concentration. Figure 9 shows an example for the changes of concentration and current efficiency with the sample the grafting yield of which is 54.6%. In order to obtain a steady state concentration, at least 3 days were necessary. The final concentration was ca. 15%. On the other hand, the current efficiency decreased gradually till it reached ca. 20%.

Both the steady state concentration and the current efficiency of the present grafted films were smaller than those of our goal as an ion-exchange membrane for the chlor-alkali cell (40 and 90%, respectively). Considering this with the electric resistance of the grafted film as shown in Figure 8, one of the reasons for the big differences between the observed values and the goal values may be based on the morphology of the grafted films. As already mentioned, the grafted film contains carboxyl functional groups mainly in the amorphous

region of the trunk polymer. When the grafting yield is increased to gain a sufficiently low electric resistance the channels among the ion clusters are produced, which inevitably enables the transport of water as well as  $\text{Na}^+$  as shown in Figure 5. This brings about the suppression of both the concentration of NaOH in the cathode cell and the efficiency of the supplied electricity.

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