

Transport of Alkali Metal Ions Against Its Concentration Gradient through 2,3-Epithiopropyl Methacrylate–Methacrylic Acid Copolymer Membrane

TAKAMASA NONAKA, HIROTOSHI MAEDA, MORIO NAKAYAMA, and HIROAKI EGAWA, *Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860 Japan*

Synopsis

Cationic exchange membranes were prepared with 2,3-epithiopropyl methacrylate (ETMA)–methacrylic acid (MAc) copolymer. Transport of Li^+ against its concentration gradient through the membranes was investigated by using the system containing HCl and LiCl (left side) and LiOH (right side). The rate of transport of Li^+ increased with increasing MAc content in the membranes with less than 56.3 mol % MAc. The rate of transport and transport fraction of Li^+ could be increased by using the copolymer membranes irradiated with ultraviolet light, because the physical and chemical structure of the membrane made of ETMA–MAc copolymer can be easily changed by irradiation with ultraviolet light. The transport in this system, where one side of the membrane in a cell was acidic and the other alkaline, was influenced significantly by the initial H^+ concentration on the acidic side.

INTRODUCTION

Transport of metal ions,^{1–5} anions,^{6,7} and organic cations⁸ against its concentration gradient through synthetic polymeric membranes with a fixed specific functional carrier has been studied by many workers. Transport of alkali metal ions against its concentration gradient through the cation exchange membranes containing carboxyl groups has been investigated, and the transport mechanism has been proposed.^{4,9}

We reported previously that poly(2,3-epithiopropyl methacrylate) (PETMA) and its copolymers were easily crosslinked by exposure of ultraviolet (UV) light (< 300 nm).¹⁰ It is considered that the ability to carry out transport of metal ions through the membranes UV-irradiated can be changed, because the physical and chemical structure (microstructure) of the membrane made of PETMA or its copolymer can easily be changed by irradiation of UV light.

The report is concerned with a transport of Li^+ against its concentration gradient through the 2,3-epithiopropyl methacrylate (ETMA)–methacrylic acid(MAc) copolymer membranes crosslinked by irradiation of UV light.

EXPERIMENTAL

Synthesis of ETMA–MAc Copolymer

ETMA was prepared by the method reported earlier.¹⁰ ETMA–MAc copolymers with various MAc contents were prepared by a solution polymeriza-

tion in 1,4-dioxane (dioxane) using azobisisobutyronitrile as an initiator at 50°C for 1.5–2 h under nitrogen atmosphere. The copolymers were purified by twice reprecipitation from dioxane–diethyl ether system and then the copolymer dioxane solution (5%) was immediately prepared without drying the copolymer.

The composition of ETMA–MAc copolymers was calculated from the sulfur content of the dried polymers determined by flask combustion method.¹¹

Preparation Method of Membrane

The membranes were made by pouring the 5% dioxane copolymer solution onto a glass plate (5 × 5 cm), allowing evaporation of solvent at room temperature for 12 h. The membranes prepared were torn off from the glass plate in water. After drying the membrane in the dark, they were irradiated at a distance of 10 cm from the UV light (< 300 nm) at room temperature for desired time. The low pressure mercury lamp, Ushio 6 W, was used as a light source for the crosslinking of the copolymers. The thickness of the membrane was 20–25 μm.

Apparatus and Measurement

Transport experiment was carried out at 30°C under magnetic stirring, using a diaphragm glass cell (22 cm³) consisting of two detachable parts. The membrane was set in the middle of the two parts of the cell, which were clamped and sealed tightly with silicon rubber packing. The effective membrane area in the cell was 4.5 cm². The concentration of metal ions in both left and right cells was determined by flame emission spectroscopy. The concentration of Cl⁻ ion in both cells was determined by the Fajans method.¹² The pH of the solution was measured with a pH meter (Model HM-20, Toa Electronic Ltd.).

Measurement of Cation Exchange Capacity of the Membranes

The dried copolymer membrane (0.25 g) was placed in a 100 cm³ glass-stoppered Erlenmeyer flask. Then 50 cm³ of 0.1 mol dm⁻³ NaOH–1 mol dm⁻³ NaCl solution was poured into the flask. The mixture was allowed to stand at 30°C for 48 h with shaking. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant with a 0.1 mol dm⁻³ HCl solution.

Measurement of Moisture Content and the Swelling Ratio of the Membrane

Moisture content of the membrane was calculated by use of the following equation:

moisture content (%)

$$= \frac{\text{wt of wet membrane (g)} - \text{wt of dry membrane (g)}}{\text{wt of dry membrane (g)}} \times 100 \quad (1)$$

The wet membrane was prepared by immersing the dry membrane into deionized water for 24 h at room temperature, followed by wiping water on the surface of the membrane with filter paper and then the membrane was weighed.

The swelling ratio of the membrane was calculated as follows:

$$\text{swelling ratio} = \frac{a' \times b' \times c'}{a \times b \times c} \quad (2)$$

where a , b , and c represent the length of two sides and the thickness of dry rectangular membrane and a' , b' , and c' represent those after immersing the membrane in 0.1 mol dm⁻³ KOH solution, respectively. The length of two sides of the rectangular membrane and its thickness was measured with a ruler and a micrometer, respectively. The value of c'/c of the copolymer membrane with low MAc content was almost the same as that of a'/a and b'/b . However, in the case of the copolymer with high MAc content, it was very difficult to determine the exact thickness of the wet membrane with a micrometer, because the copolymer with high MAc content swelled considerably in 0.1 mol dm⁻³ KOH solution and the membrane was very soft. In this case, the swelling ratio was calculated by cubing the ratio of the length of a side of the dry membrane to that after immersing it into 0.1 mol dm⁻³ KOH solution at room temperature.

RESULTS AND DISCUSSION

Synthesis of ETMA-MAc Copolymer with Various MAc Contents

Some synthesized ETMA-MAc copolymers with various MAc contents are listed in Table I. The former and latter numbers in the abbreviation of the membrane such as E8M2 or E7M3 in Table I represent the vol % of ETMA and MAc in the feed before copolymerization respectively.

All these copolymers became insoluble in any organic solvent after they were once dried. So 5% copolymer dioxane solution was prepared without

TABLE I
Synthesis of ETMA-MAc Copolymer with Various MAc Contents^a

Abbreviation	Feed (cm ³)		1,4-dioxane (cm ³)	ETMA/MAc in copolymer (mol ratio)
	ETMA	MAc		
E5M5	5.0	5.0	20	27.0/73.0
E6M4	6.0	4.0	20	36.5/63.5
E6.5M3.5	6.5	3.5	20	40.0/60.0
E7M3	7.0	3.0	20	43.7/56.3
E7.5M2.5	7.5	2.5	20	48.0/52.0
E8M2	8.0	2.0	20	52.4/47.6
E8.4M1.6	8.4	1.6	20	56.5/43.5
E8.5M1.5	8.5	1.5	20	58.0/42.0
E9M1	9.0	1.0	20	63.1/36.9

^a Polymerization was carried out at 50°C for 2 h.

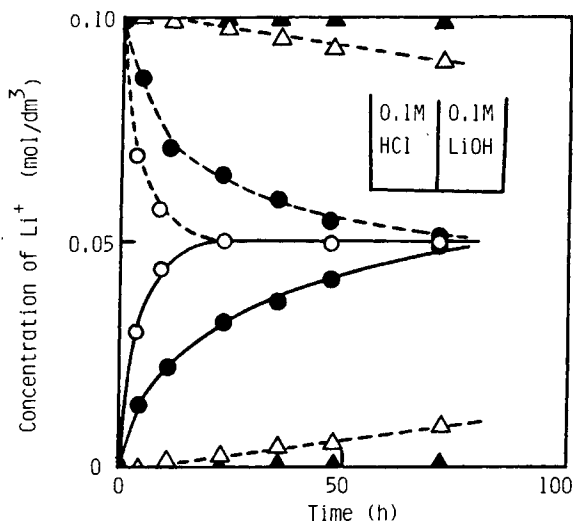


Fig. 1. Transport of Li^+ through the membrane consisting of various compositions: (—) L side, (---) R side. Membrane: (○) E8M2; (●) E8.4M1.6; (△) E8.5M1.5; (▲) E9M1.

drying the copolymers and then the membranes were made by using the solution.

The transport of Li^+ through these membrane was investigated by using the system shown in Figure 1. In the case of the E9M1 membrane which has the ETMA/Mac mol ratio of 63.1/36.9 in copolymer, Li^+ was hardly transported through the membrane. The ETMA-Mac copolymer membranes with Mac content ranging from 47.6 to 42.0 mol % transported Li^+ . In the case of these membranes, the rate of transport of Li^+ through the membrane increased with increasing Mac contents in the membrane. The ETMA-Mac copolymer membranes which have more than 52.0 mol % Mac content were broken after setting the membrane at the middle of the two parts of the cell. This break of the membrane is attributed to the high swelling in LiOH solution.

The transport of Li^+ through the E8M2 membrane (52.4/47.6 mol ratio) was investigated by using various systems as shown in Figure 2. In the system containing 0.1 mol dm^{-3} HCl [left (L) side] and 0.1 mol dm^{-3} LiOH [right (R) side], the rate of the transport of Li^+ through the membrane is higher than that in the system containing no HCl in the L side. The transport of Li^+ through the membrane was also investigated by using the systems containing HCl or no HCl (L side) and LiCl (R side). In both systems, no Li^+ was transported from the R side to L side through the membrane. These results suggest that it is necessary to form the carboxylate for the transport of Li^+ through the membrane.

Transport of Alkali Metal Ions Against Its Concentration Gradient

The transport of Li^+ through the copolymer membranes with various Mac contents was carried out by use of the system having 0.05 mol dm^{-3} HCl-0.05

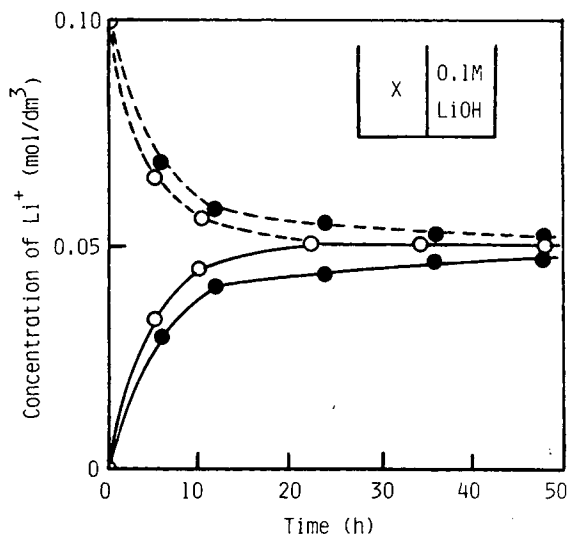


Fig. 2. Transport of Li^+ through the membrane: membrane, E8M2; (—) L side, (---) R side; (○) X = 0.1M HCl; (●) X = H_2O .

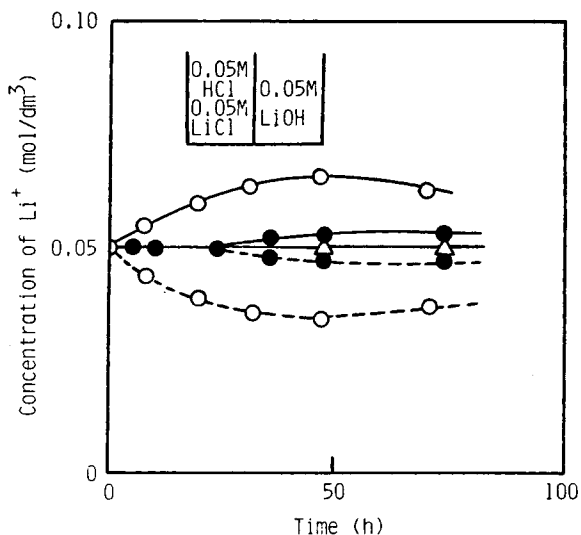


Fig. 3. Change in concentration of Li^+ through the membrane: (—) L side; (---) R side. Membrane: (○) E8M2; (●) E8.5M1.5; (△) E9M1.

mol dm^{-3} LiCl (L side) and 0.05 mol dm^{-3} LiOH (R side) (Fig. 3). E8M2 membrane transported Li^+ most rapidly from R side to L side. Consequently, the concentration of Li^+ in the L side became higher than that in the R side. This means that Li^+ was transported against its concentration gradient from R side to L side. E8.5M1.5 membrane transported Li^+ slightly and E9M1 membrane did not transport Li^+ at all.

Figure 4 shows the tentative transport mechanism during the transport of metal ions against its concentration gradient through the membrane. When

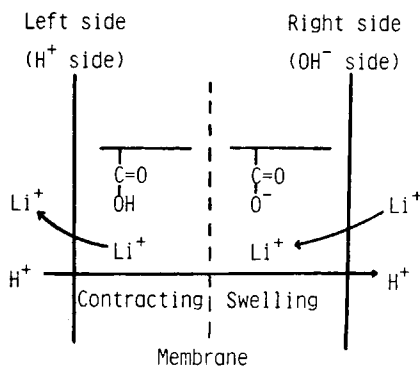


Fig. 4. Tentative mechanism of the transport of Li^+ ions.

one side was alkaline and the other side acidic across the membrane, the carboxyl groups in the membrane dissociate in the alkaline side (OH^- side), and the metal ions are incorporated into the membrane by the ion exchange between H^+ ions in the carboxyl groups and the metal ions on the alkaline side. The metal ions are migrated by the carboxyl groups fixed to the membrane matrix from the R side to the L side. When the carboxylate reached the left side (H^+ side), carboxylate changed to carboxyl groups, and the alkali metal ions were released in the left side cell. As a result of this mechanism, alkali metal ions were transported from the alkaline side to acidic side.

Effect of UV Irradiation on Transport of Li^+

Effect of irradiation of UV light on the transport of metal ions against its concentration gradient through the membrane was investigated by using E8M2, E7M3, and E6.5M3.5 membranes. The results are shown in Figures 5 and 6. The membranes were irradiated at room temperature for 0–4 h prior to use. E7M3 and E6.5M3.5 membrane, which were irradiated for more than 2 and 4 h, respectively, could also be used without breaking for this experiment. This is attributed to the photocrosslinking of ETMA–MAc copolymers by UV irradiation. In all these experiments, the transport of Li^+ against its concentration gradient through the membranes was observed. In the case of E8M2 membrane [Fig. 5(A)], Li^+ was transported most rapidly through the membrane irradiated for 1 h, and the rate of transport of Li^+ decreased with increasing irradiation time. In the membrane nonirradiated, it was found that Li^+ concentration in the L side started to decrease after 50 h. This is simply due to a diffusive transport caused by the concentration gradient of metal ions. As shown in Figures 5(A) and 5(B), the rate of transport of Li^+ through the membrane increased with increasing MAc content of the copolymer membrane. E7M3 membrane irradiated for 3 h transported Li^+ most rapidly, and the highest transport fraction was obtained [Fig. 5(B)]. In the case of E6.5M3.5 copolymer membrane (Fig. 6), the Li^+ concentration in the L side decreased remarkably after 25 h. It is considered that this phenomenon was brought about by backtransfer of transported Li^+ from the L side to R side caused by the concentration gradient owing to the high swelling of the

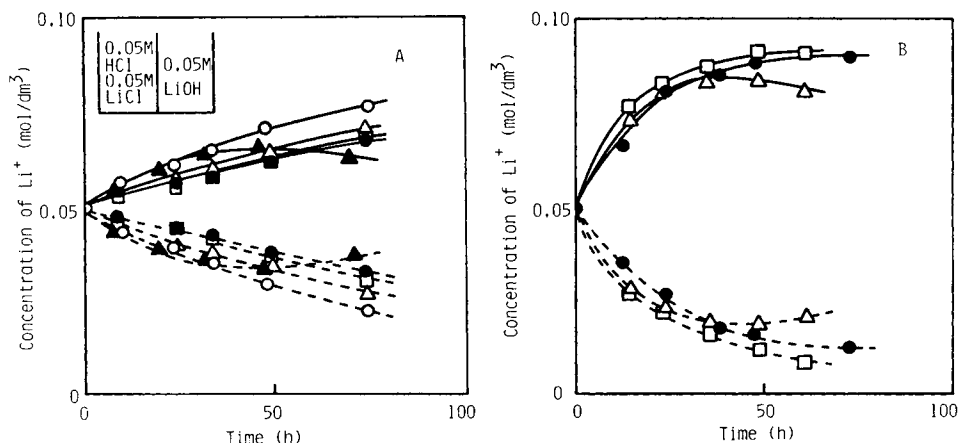


Fig. 5. Change in concentration of Li^+ through the membrane: (—) L side; (---) R side. (A) Membrane E8M2: (\blacktriangle) nonirradiated; (\circ) UV-irradiated for 1 h; (\triangle) UV-irradiated for 2 h; (\square) UV-irradiated for 3 h; (\bullet) UV-irradiated for 4 h. (B) Membrane E7M3: (\triangle) UV-irradiated for 2 h; (\square) UV-irradiated for 3 h; (\bullet) UV-irradiated for 4 h.

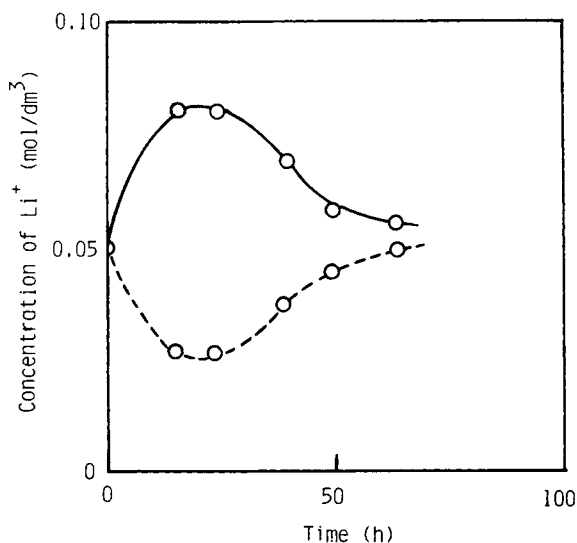


Fig. 6. Change in concentration of Li^+ through the membrane: membrane, E6.5M3.5 UV-irradiated for 4 h; (—) L side; (---) R side.

membrane with high MAc content. From these results, it was found that the copolymer membranes with high MAc content can also be used without breaking by irradiation of UV light and the transport rate and the transport fraction of Li^+ could be increased by using the E7M3 copolymer membranes irradiated with UV light for 3–4 h.

Properties of the ETMA-MAc Copolymer Membrane

In order to clarify the relation between the transport of alkali metal ions against its concentration gradient and the properties of the membrane, the

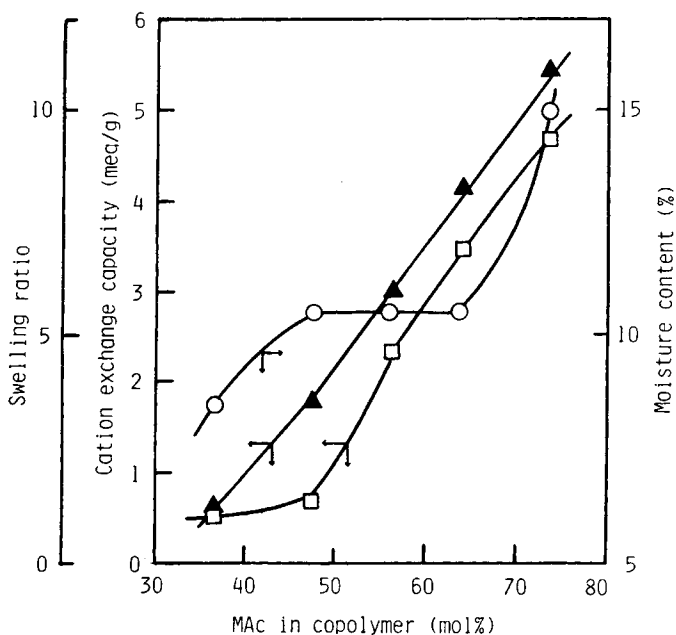


Fig. 7. Cation exchange capacity, swelling ratio, and moisture content of ETMA-MAc copolymer membrane: (▲) cation exchange capacity; (□) swelling ratio; (○) moisture content.

various properties of the membrane were measured. Figure 7 shows the cation exchange capacity, moisture content, and swelling ratio of the copolymer membranes with various MAC contents. The cation exchange capacity and the swelling ratio increased with increasing MAC content of the membrane. The moisture content of E8M2 and E7M3 copolymer membrane was almost the same and the moisture content of the E5M5 and E9M1 copolymer membrane is significantly lower and higher than that of the E8M2-E6M4 copolymer membranes, respectively. The fact that Li^+ could not be transported through the E9M1 membrane is attributed to the low cation exchange capacity and low swelling. As mentioned earlier, the membranes nonirradiated with MAC content of more than 52.0% were broken after setting because of the high swelling. On the other hand, we have reported that the photocrosslinking of PETMA and its copolymer with UV light occurred in a few minutes^{10,13}. So the cation exchange capacity, moisture content, and swelling ratio of the E8M2 and E7M3 membranes irradiated with UV light for varying time were also measured. The results are shown in Figures 8 and 9. The cation exchange capacity of the membranes increased slightly with increasing irradiation time, whereas the moisture content and swelling ratio decreased with increasing irradiation time. The increase of cation exchange capacity is probably due to the $-\text{SH}$ groups formed in the side reaction of the photocrosslinking by UV irradiation.¹⁰ The decrease of moisture content and swelling ratio is attributed to the photocrosslinking of the membrane by UV irradiation.

Effect of pH on the Transport of Li^+

Figure 10 shows the pH change in both L side and R side with time during the transport of Li^+ against its concentration gradient through the E8M2 and

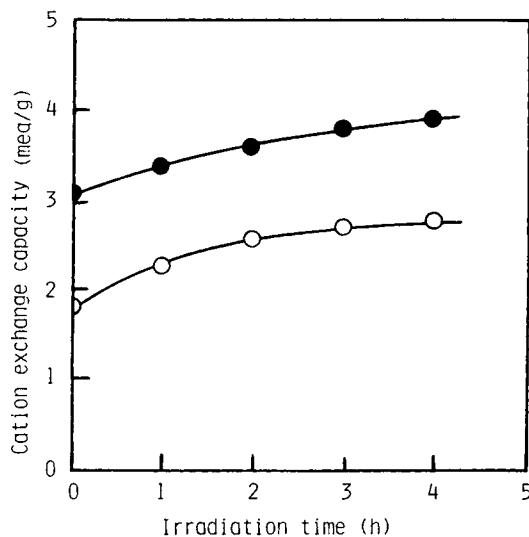


Fig. 8. Effect of UV irradiation on the cation exchange capacity. Membrane: (●) E7M3; (○) E8M2.

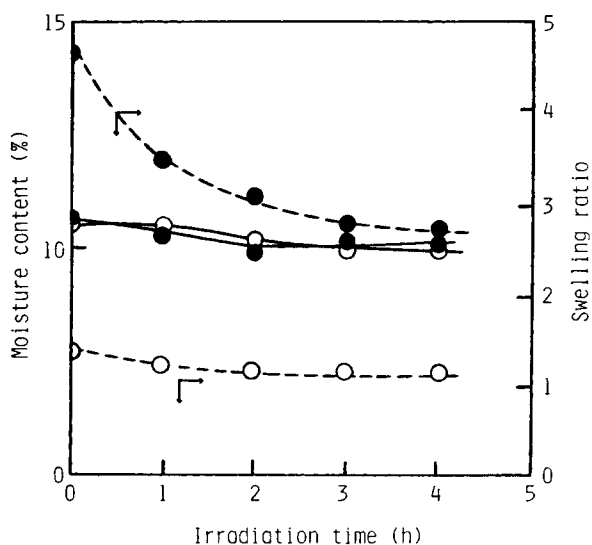


Fig. 9. Effect of UV irradiation on the moisture content and the swelling ratio: (—) moisture content; (---) swelling ratio. Membrane: (●) E7M3; (○) E8M2.

E7M3 membrane. In the case of E8M2 membrane irradiated for 1 h, the pH in both sides hardly changed up to 200 h, whereas, in the case of E8M2 membrane nonirradiated, the pH became almost the same after about 50 h. This result suggests that the diffusion of H^+ and OH^- ions across the membrane was depressed by irradiation of the membrane with UV light. The time at which pH difference disappeared corresponds to the time at which the reverse diffusion of Li^+ started by concentration gradient [Fig. 5(A)]. In the case of E7M3 membrane irradiated for 4 h which showed the high transport rate, the pH in both sides became almost the same after about 120 h. From

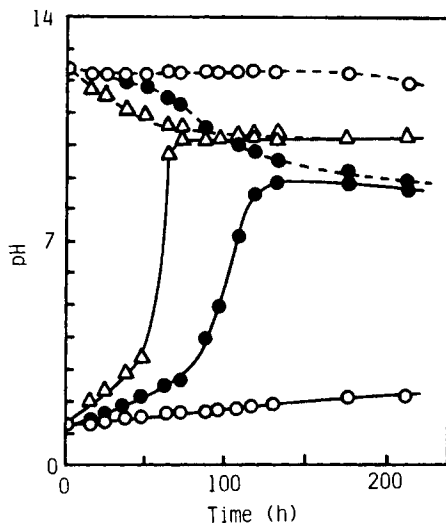


Fig. 10. Change of pH on both side: (—) L side; (---) R side. Membrane: (Δ) E8M2 nonirradiated; (\circ) E8M2 UV-irradiated for 1 h; (\bullet) E7M3 UV-irradiated for 4 h.

these results, it was found that high transport fraction was brought about by the persistence of the large pH difference between the L and R sides for a long period.

Effect of the initial pH in the L side on the transport of Li^+ was also investigated by using the system shown in Figure 11. The E8M2 membrane irradiated for 1 h was used for this experiment. When the initial H^+ concentration in the L side was 0.5 mol dm^{-3} (pH 0.3), no transport of Li^+ occurred. The highest rate of transport of Li^+ was obtained when the acidic

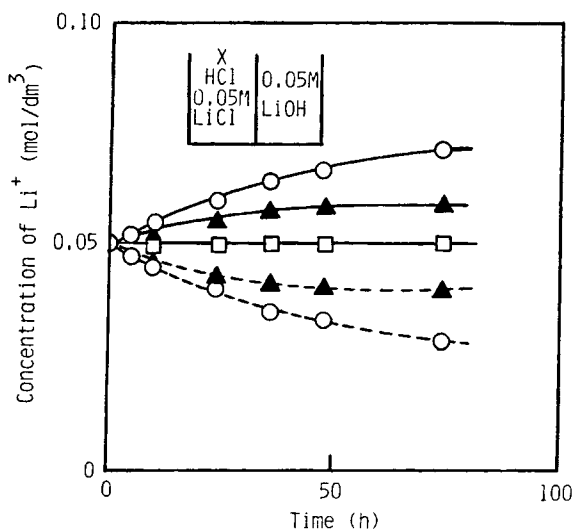


Fig. 11. Effect of the initial pH in the L side on the transport of Li^+ : membrane, E8M2 UV-irradiated for 1 h; (—) L side; (---) R side. X = : (\square) 0.5M (pH 0.3); (\circ) 0.05M (pH 1.3); (\blacktriangle) 0.005M (pH 2.3).

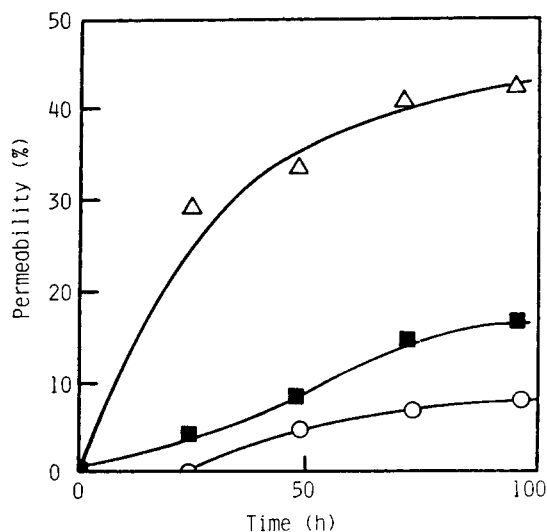


Fig. 12. Permeation of Cl^- through the membrane: (Δ) E8M2 nonirradiated; (\circ) E8M2 UV-irradiated for 1 h; (\blacksquare) E7M3 UV-irradiated for 4 h.

equivalent in the L side was almost the same as the alkaline equivalent in the R side. These results are due to the fact that under these conditions the L side and R side can be kept acidic pH and alkaline pH, respectively, during a long transport period.

Permeability of Cl^- through the Copolymer Membrane

Figure 12 shows the permeability of Cl^- from L side to R side through the membranes of E8M2 nonirradiated, E8M2 irradiated for 1 h, and E7M3 irradiated for 4 h. As shown in Figure 12, Cl^- permeated rapidly through the E8M2 membrane nonirradiated, whereas it permeated slowly through the E8M2 membrane irradiated for 1 h and the E7M3 membrane irradiated for 4 h. These results show that the diffusion of Cl^- from the L side to R side was depressed by UV irradiation of the copolymer membrane. This implies that the dense membranes were formed by the photocrosslinking of the membrane by UV irradiation. We have observed that Li^+ , which was transported against its concentration gradient through the E8M2 membrane nonirradiated from the R side to L side, was backtransferred by the concentration gradient of metal ions from the L side to R side after 50 h [Fig. 5(A)]. From these results, it is necessary to make the diffusion of Cl^- difficult across the membrane from the L side to the R side to obtain high transport fraction.

CONCLUSION

In order to obtain the membrane with high ability of transport of metal ions against its concentration gradient, it is necessary to (1) increase the content of carrier such as carboxyl group in the membrane in the composition range at which the membrane can be used without breaking, (2) make the membrane dense for H^+ and OH^- not to diffuse simply through the membrane by the concentration gradient, and (3) depress the diffusion of anion

such as Cl^- into the membrane. The membranes with high MAc content, which were broken owing to high swelling, could also be used without breaking for transport experiment by irradiation of UV light. For the preparation of the ETMA-MAc copolymer membranes which show high ability of transport against its concentration gradient, the irradiation of the membrane with UV light is one of the best methods because the photocrosslinking of the membrane can be easily carried out under mild conditions and the microstructure of the membrane can be varied delicately by irradiation of UV light.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

References

1. T. Shimizu, M. Yoshikawa, M. Hasegawa, and K. Kawakatsu, *Macromolecules*, **14**, 170 (1981).
2. T. Shimizu, M. Yoshikawa, and B. Ohtani, *Macromolecules*, **14**, 506 (1981).
3. T. Uragami, R. Nakamura, and F. Sugihara, *Polymer*, **24**, 559 (1983).
4. T. Uragami, S. Watanabe, R. Nakamura, F. Yoshida, and M. Sugihara, *J. Appl. Polym. Sci.*, **28**, 1613 (1983).
5. W. Fukuda, S. Suzue, and H. Kakiuchi, *Nippon Kagaku Kaishi*, **1983**, 880.
6. N. Ogata and K. Sanui, *Kobunshi Ronbunshu*, **38**, 583 (1981).
7. N. Ogata, K. Sanui, and H. Fujimura, *J. Appl. Polym. Sci.*, **26**, 4149 (1981).
8. T. Uragami, S. Watanabe, and M. Sugihara, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1193 (1982).
9. T. Uragami, S. Watanabe, R. Nakamura, and M. Sugihara, *Polym. Bull.*, **7**, 71 (1982).
10. H. Egawa and T. Nonaka, *Kobunshi Ronbunshu*, **35**, 21 (1978).
11. Yuki Biryō Bunseki Kenkyū Kōndaikai Henshu, Yuki Biryō Teiryō Bunseki, Nankōdo, Tokyo, 1969, p. 383.
12. K. Sugahara and T. Michino, *Teiryō Bunseki*, Asakura, Tokyo 1977, p. 98.
13. H. Egawa, T. Nonaka, T. Hirusawa, M. Tsunooka, and M. Tanaka, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2597 (1983).

Received November 4, 1986

Accepted February 10, 1987