

# Transport of Alkali Metal and Alkali Earth Metal Ion Against Their Concentration Gradient through 2,3-Epithiopropyl Methacrylate–Methacryloyloxyethyl Phosphoric Acid Copolymer Membranes

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## Synopsis

Cationic exchange membranes were prepared with 2,3-epithiopropyl methacrylate (ETMA)–methacryloyloxyethyl phosphoric acid (MP) copolymers. Transport of alkali metal and alkali earth metal ion against their concentration gradient through the UV-irradiated and nonirradiated membranes was investigated by using the system, where one side (L side) of the membrane in a diaphragm cell was acidic and the other (R side) alkaline or neutral, under various conditions. The ETMA–MP copolymer membranes transported rapidly alkali metal and alkali earth metal ion against their concentration gradient and the maximum transport fraction was more than 95%. The transport rate and transport fraction of metal ions was greatly affected by the composition of the copolymer membranes and  $H^+$  concentration in the L side. The transport selectivity between alkali metal ions was increased by using the E8P2 membrane UV-irradiated, but the degree of increase in the selectivity was not large.  $Ca^{2+}$  was transported more rapidly than  $Li^+$  against their concentration gradient.

## INTRODUCTION

In the previous articles,<sup>1,2</sup> we have reported that  $Li^+$  could be transported against its concentration gradient through the membrane made of ETMA–methacrylic acid (MAc) copolymer, the transport rate and transport fraction of  $Li^+$  could be increased by using the copolymer membranes irradiated with UV light, and the transport selectivity between alkali metal ions could also be increased by using the membrane irradiated with UV light, although the transport rate of alkali metal ions was decreased. The transport rate of alkali metal ions through these ETMA–MAc membranes which have carboxyl groups as carrier was not always high. The synthesis of the membranes containing phosphoric acid groups and the transport of metal ions through the membranes have been little reported. In this research, the membranes were prepared with ETMA–MP copolymer carrying phosphoric acid groups and the transport of alkali metal and alkali earth metal ion through the membranes was investigated. In addition, the effect of irradiation of UV light and drying temperature of the membranes on the selective transport of alkali metal and alkali earth metal ion through the ETMA–MP copolymer membranes was investigated.

## EXPERIMENTAL

### Synthesis of ETMA-MP Copolymers

ETMA was prepared by the method reported earlier.<sup>3</sup> MP was given by Nippon Oil Company Ltd. and it was used without further purification. ETMA-MP copolymers with various MP contents were prepared by a solution polymerization in *N,N*-dimethylformamide (DMF) using azobisisobutyronitrile as an initiator at 50°C for 3–7 h. The composition of ETMA-MP copolymers was calculated from the phosphorus content of the dried copolymers. The phosphorus content was determined as follows: Dried membrane (0.1 g) and 70% nitric acid (10 mL) were placed in a Kjeldahl flask and the mixture was heated until white steam came out, and then was cooled. After that, 60% perchloric acid (10 mL) was added to this solution, and the mixture was heated until the solution became transparent. The concentration of phosphoric acid in the resulted solution was determined by phosphovanadomolybdate method.<sup>4</sup>

### Preparation Method of Membranes

The membranes were made by pouring 3 mL of ETMA-MP copolymer DMF solution (5%) into a flat laboratory dish (4.8 cm diameter) immediately after polymerization and the solvent was allowed to evaporate at 50°C for the desired time, because the ETMA-MP copolymers became insoluble in any organic solvent when it was precipitated in organic solvent and once dried. In the case of studying the effect of the drying temperature on the transport of Li<sup>+</sup>, the membranes were prepared by drying at 30, 40, 50, and 60°C. The membranes prepared were removed from the dish in water-methanol solution. The thickness of the wet membrane was 20–40 μm. After drying the membrane in the dark, the membranes were placed parallel to the lamp and irradiated at a distance of 10 cm from the UV light (< 300 nm) at room temperature for the desired time in air. The 6-W low pressure mercury lamp (190 × 15 mmφ) (Ushio OLO 6AB6) was used as a light source for the photocrosslinking of the copolymers.

### Apparatus and Measurement

Transport experiments were carried out at 30°C under magnetic stirring, using a diaphragm glass cell (22 cm<sup>3</sup>) 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 3.8 cm<sup>2</sup>. The concentration of metal ions in both left and right cells was determined by flame emission spectroscopy. 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 cm<sup>3</sup> glass-stoppered Erlenmeyer flask. Then 50 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> NaOH–1 mol dm<sup>-3</sup> NaCl solution was poured into the flask. The mixture was shaken at 30°C for 48 h. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant with a 0.1 mol dm<sup>-3</sup> HCl solution. Ion exchange capacity was calculated as follows:

$$\text{cation exchange capacity (meq/g)} = p/w \quad (1)$$

where  $p$  and  $w$  are the amount of alkali metal ion adsorbed on the membrane and the weight of the membrane, respectively.

### Measurement of Water Content and the Swelling Ratio of the Membrane

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

$$\text{water content (\%)} = \frac{\text{wt wet membrane (g)} - \text{wt dry membrane (g)}}{\text{wt dry membrane (g)}} \times 100 \quad (2)$$

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; then the membrane was weighed. The membrane was immersed in a deionized water for 24 h and the swelling ratio of the membrane was calculated as follows:

$$\text{swelling ratio} = v'/v \quad (3)$$

where  $v$  and  $v'$  are the volume of dry and wet membrane, respectively.

### Transport Rate and Transport Fraction

The transport rate and transport fraction were defined as follows:

$$\text{transport rate (mmol h}^{-1} \text{ cm}^{-2}\text{)} = \frac{m_t}{t \times s} \quad (4)$$

where  $m_t$ ,  $t$ , and  $s$  are the transported alkali metal ion (mmol) to the L side during the initial transport, the transport time (h), and the effective membrane area (cm<sup>2</sup>), respectively;

$$\text{transport fraction (\%)} = \frac{C_{\max} - C_{L0}}{C_{R0}} \quad (5)$$

where  $C_{\max}$ ,  $C_{L0}$ , and  $C_{R0}$  are the maximum concentration of alkali metal ion in the L side, the initial concentration of alkali metal ion in the L side, and the initial ion concentration in the R side, respectively.

## RESULTS AND DISCUSSION

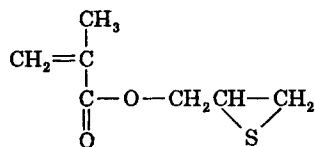
### Synthesis of ETMA–MP Copolymers with Various MP Contents

The synthesized ETMA–MP copolymers with various MP contents are listed in Table I. The former and latter numbers in the abbreviation of the membrane

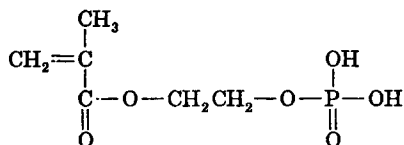
TABLE I  
Characterization of ETMA-MP Copolymer Membranes with Various MP Contents

Abbreviation of copolymer membrane	Feed			ETMA/MP in copolymer (mol ratio)	Cation exchange capacity (meq/g)	Water content <sup>c</sup> (%)	Swelling ratio <sup>d</sup>
	ETMA <sup>a</sup>	MP <sup>b</sup> (cm <sup>3</sup> )	DMF				
E9P1	1.8	0.2	20	93.0/7.0	0.73	20.0	1.00
E8P2	1.6	0.4	20	85.5/14.5	1.68	88.5	1.21
E7.5P2.5	1.5	0.5	20	81.9/18.1	2.12	98.1	1.26
E7P3	1.4	0.6	20	77.7/22.3	2.38	105.1	1.29
E6P4	1.2	0.8	20	62.7/37.3	3.68	112.2	1.32

<sup>a</sup> 2,3-Epithiopropyl methacrylate:



<sup>b</sup> Methacryloyloxyethyl phosphoric acid:



<sup>c</sup> 100 (weight of wet resin - weight of dry resin)/weight of dry resin.

<sup>d</sup> Volume of wet resin in water/volume of dry resin.

such as E8P2 and E7P3 in Table I represent the volume ratio of ETMA and MP in the feed before copolymerization, respectively. The time necessary for copolymerization increased with increasing MP content in feed. All these copolymers became insoluble in any organic solvent after they were once dried. The properties of the ETMA-MP copolymer membranes are also shown in Table I.

The cation exchange capacity, water content, and swelling ratio increased with increasing content of MP in the copolymer membranes.

### Transport of Li<sup>+</sup> against Its Concentration Gradient

The transport of Li<sup>+</sup> through the copolymer membranes with various MP contents was carried out by use of the system having 0.05 mol dm<sup>-3</sup> HCl-0.05 mol<sup>-3</sup> LiCl (L side) and 0.05 mol dm<sup>-3</sup> LiOH (R side) (Figs. 1 and 2).

The E9P1 membrane hardly transported Li<sup>+</sup> from R side to L side. This is attributed to very small amount of phosphoric acid groups and to a small swelling of the membrane (Table I). The E8P2 and E7P3 membranes transported more rapidly Li<sup>+</sup> from L side to R side than the E6P4 membrane against its concentration gradient. In the case of the E8P2 and E7P3 membranes, it took about 20 and 8 h for Li<sup>+</sup> in the L side to reach the maximum concentration, respectively. In the case of the E6P4 membrane, Li<sup>+</sup> concentration in the L

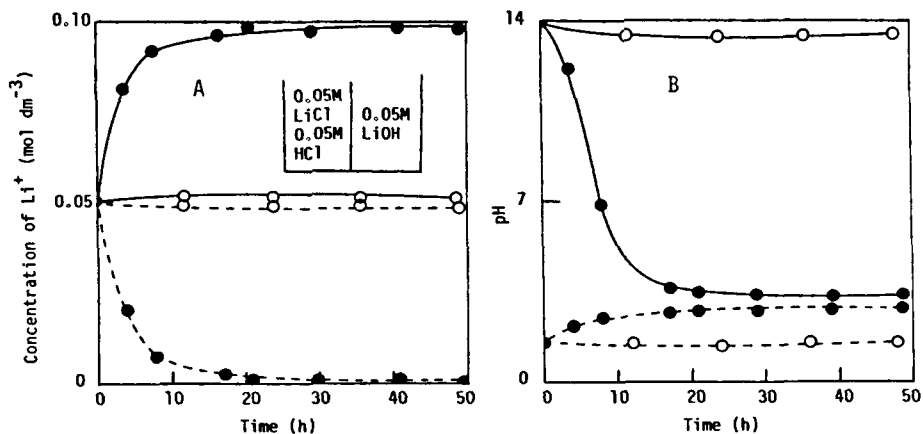


Fig. 1. Changes in concentration of  $\text{Li}^+$  through the membranes and pH on both sides: (A) change of  $\text{Li}^+$  concentration; (B) change of pH. Membrane: (O) E9P1; (●) E8P2: (—) L side; (---) R side.

side began to decrease after 3 h and the maximum  $\text{Li}^+$  concentration in the L side did not exceed  $0.072 \text{ mol dm}^{-3}$ . This is due to a reverse diffusion of transported  $\text{Li}^+$  from the L side to R side caused by the concentration gradient of  $\text{Li}^+$  owing to the highest swelling of the E6T4 membrane.

Figures 1(B) and 2(B) show the pH changes of both L side and R side with time during transport experiment. In the case of the E9P1 membrane, the pH of both sides hardly changed for 50 h. This indicates that  $\text{H}^+$  and  $\text{OH}^-$  did not diffuse across the membrane.

In the case of the E8P2 and E7P3 membranes, the pH of both sides became very close after 20 and 12 h, respectively. In the case of the E6P4 membrane, the pH of both sides became almost the same after 5 h. This indicates that  $\text{H}^+$

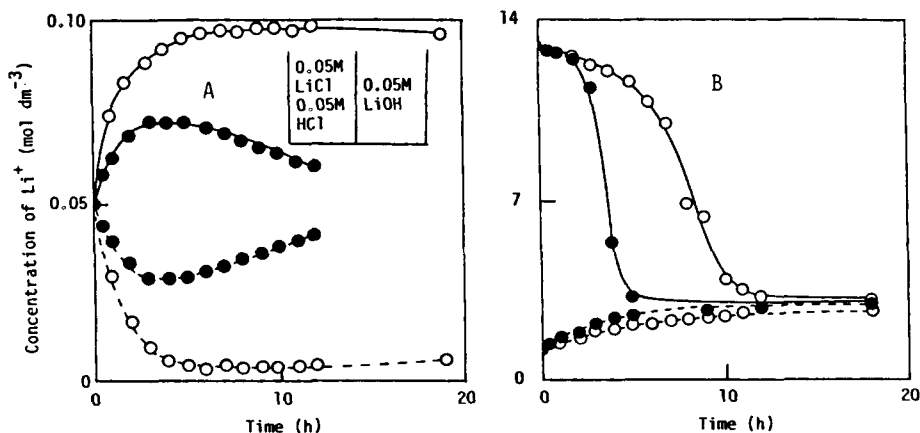


Fig. 2. Changes in concentration of  $\text{Li}^+$  through the membranes and pH on both sides: (A) change of  $\text{Li}^+$  concentration; (B) change of pH. Membrane: (O) E7P3; (●) E6P4: (—) L side; (---) R side.

diffuse easily across the E6P4 membrane because of high swelling of the membrane.

### Effect of $H^+$ Concentration in the L Side on the Transport of $Li^+$

The transport of  $Li^+$  through the E7P3 membrane was measured by varying the  $H^+$  concentration in the L side (Fig. 3). The initial concentration of lithium hydroxide in the R side kept constant at  $0.05 \text{ mol dm}^{-3}$  in all systems and that of hydrochloric acid in the L side was changed from 0.01 to  $0.5 \text{ mol dm}^{-3}$ . The pH change in both sides was also measured [Fig. 3(B)].

The transport rate and transport fraction increased with increasing  $H^+$  concentration up to  $0.1 \text{ mol dm}^{-3}$  and they decreased by using  $0.5 \text{ mol dm}^{-3}$  HCl. When initial  $H^+$  concentration in the L side is smaller than  $OH^-$  concentration in the R side, both L and R sides became alkaline after about 5 h, whereas when  $0.5 \text{ mol dm}^{-3}$  HCl was used, both L and R sides became acidic rapidly. This is attributed to the rapid diffusion of  $H^+$  from the L side to the R side owing to the high its concentration gradient. In the case of 0.05 and  $0.1 \text{ mol dm}^{-3}$  HCl [Figs. 2(B) and 3(B)] in which the high transport fraction of  $Li^+$  was observed, both sides became acidic and the larger pH difference between R side and L side persisted for a longer period compared with that in other cases.

### Selective Transport of Alkali Metal Ions Through the ETMA-MP Copolymer Membranes

In the previous articles,<sup>1,2</sup> we have reported that the transport selectivity between alkali metal ions could be increased by using UV-irradiated ETMA-MAc copolymer membranes and the selectivity increased with increasing irradiation time up to 2–3 h, although the transport rate of alkali metal ions decreased with increasing time of UV irradiation.

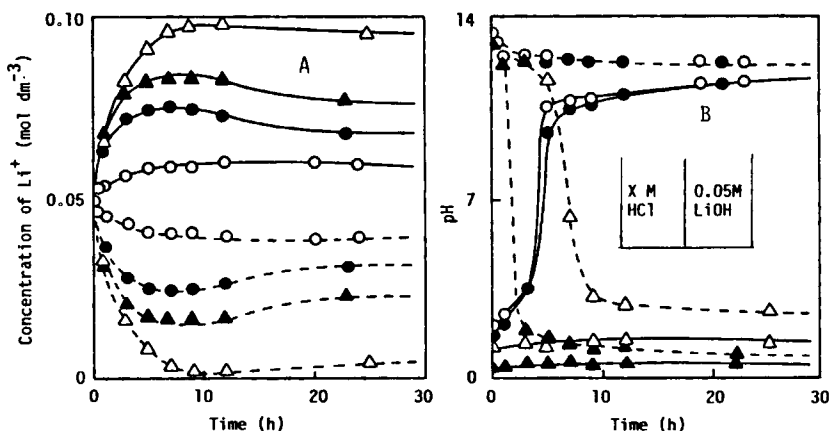


Fig. 3. Changes in concentration of  $Li^+$  through the membranes and pH on both sides: (A) change of  $Li^+$  concentration; (B) change of pH. Membrane: E7P3: (—) L side; (---) R side. HCl concentration in the L side ( $\text{mol dm}^{-3}$ ): (○) 0.01; (●) 0.025; (△) 0.1; (▲) 0.5.

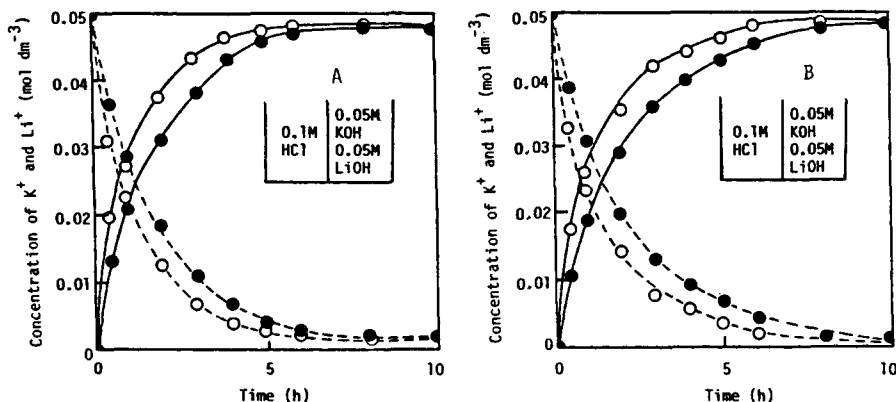


Fig. 4. Changes in concentration of  $K^+$  and  $Li^+$  on the two sides of the membrane: (A) E7P3 nonirradiated; (B) E7P3 UV irradiated for 16 h: (—) L side; (---) R side: (○)  $K^+$ ; (●)  $Li^+$ .

The effect of UV irradiation on the selective transport of alkali metal ions was investigated by using the E7P3 and E8P2 membranes UV-irradiated for 16 h and nonirradiated (Figs. 4 and 5). The L side was  $0.1 \text{ mol dm}^{-3}$  HCl solution and the R side was an aqueous solution containing both  $0.05 \text{ mol dm}^{-3}$  KOH and  $0.05 \text{ mol dm}^{-3}$  LiOH solution. In both membranes,  $K^+$  was transported more rapidly than  $Li^+$ . It took about 10 h for each alkali metal ion in the L side to reach the maximum concentration through the E7P3 membrane, whereas it took above 80 h through the E8P2 membrane. In the case of the E8P2 membrane, the large difference in the transport rate between the nonirradiated and irradiated membrane was found (Fig. 5). The transport rate of alkali metal ions through the irradiated E7P3 membrane was slightly smaller than that through the membranes nonirradiated.

The transport selectivity of  $Na^+/Li^+$  and  $K^+/Na^+$  through the E7P3 membranes UV-irradiated and nonirradiated was also investigated by using the same system as that of  $K^+/Li^+$ . The transport selectivity of the alkali metal ions through the membrane was calculated from the following equation:

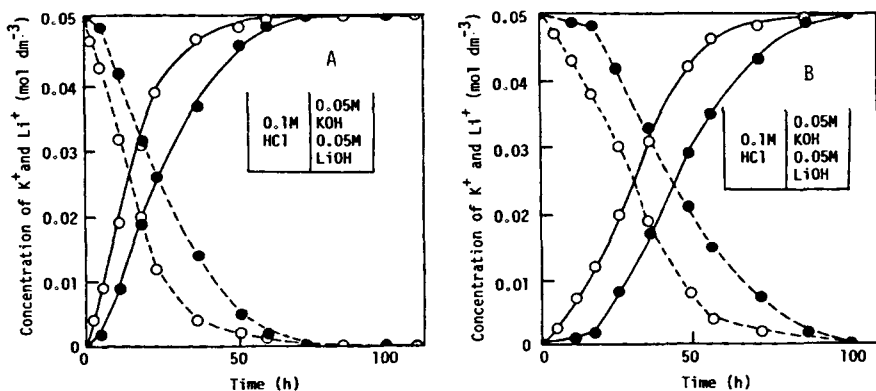


Fig. 5. Changes in concentration of  $K^+$  and  $Li^+$  on the two sides of the membrane: (A) E8P2 nonirradiated; (B) E8P2 UV irradiated for 16 h: (—) L side; (---) R side: (○)  $K^+$ ; (●)  $Li^+$ .

$$\text{transport selectivity} = \frac{M_{1t}^+/M_{10}^+}{M_{2t}^+/M_{20}^+} \quad (6)$$

where  $M_{1t}^+$  and  $M_{2t}^+$  are the concentrations of each alkali metal ion in the L side at the time when the concentration of alkali metal ion which was transported faster became the same on both sides and where  $M_{10}^+$  and  $M_{20}^+$  are the initial concentrations of each alkali metal ion in the R side. The transport selectivity of  $K^+/Na^+$ ,  $Na^+/Li^+$ , and  $K^+/Li^+$  through the membrane UV nonirradiated and irradiated were shown in Table II. All the transport selectivities of  $K^+/Na^+$ ,  $Na^+/Li^+$ , and  $K^+/Li^+$  were more than unity. These results show that the transport rate of alkali metal ions from the alkaline side to the acidic side through the membranes is given in the following order:

$$K^+ > Na^+ > Li^+$$

It is known that the alkali metal ions are hydrated in an aqueous solution and the order of the size of these hydrated ions is as follows:

$$Li^+ > Na^+ > K^+$$

Accordingly, the order of transport rate is inversely proportional to the size of the hydrated ions. Table II also indicates that the transport selectivity for alkali metal ions through the E7P3 membrane could hardly be increased by UV irradiation of the membrane. However, the transport selectivity of  $K^+/Li^+$  through the E8P2 membrane UV-nonirradiated and irradiated were 1.89 and 2.29, respectively. Thus the higher selectivity of  $K^+/Li^+$  was obtained with the E8P2 membrane irradiated, although the transport rate of alkali metal ions through the membrane became small.

### Effect of Drying Temperature of the Membranes on the Transport Rate and Selective Transport

The selective transport of  $K^+/Li^+$  through the E7.5P2.5 membranes dried at various temperatures was studied by using the system containing 0.1 mol

TABLE II  
Selectivity of Alkali Metal Ions through the ETMA-MP Copolymer Membranes

Expt no.	Membrane	Selectivity		
		$K^+/Na^+$	$Na^+/Li^+$	$K^+/Li^+$
1	E7P3 nonirradiated	1.19	1.16	1.35
2	E7P3 irradiated	1.22	1.16	1.44
3	E8P2 nonirradiated	—	—	1.89
4	E8P2 irradiated	—	—	2.29



TABLE III  
Transport Rate, Selectivity, and Transport Fraction, of Alkali Metal Ion through  
the ETMA-MP Copolymer Membranes Dried at Various Temperatures

Membrane	Temp (°C)	Initial transport rate (mmol h <sup>-1</sup> cm <sup>-2</sup> )		Ratio of initial transport rate (K <sup>+</sup> /Li <sup>+</sup> )	Transport fraction (%)	
		Li <sup>+</sup>	K <sup>+</sup>		Li <sup>+</sup>	K <sup>+</sup>
E7.5P2.5	30	0.153	0.200	1.31	96.4	96.2
	40	0.153	0.194	1.26	97.0	99.8
	50	0.141	0.190	1.35	100.0	98.8
	60	0.116	0.163	1.41	98.4	99.6

dm<sup>-3</sup> HCl (L side) and 0.05 mol dm<sup>-3</sup> LiOH-0.05 mol dm<sup>-3</sup> KOH (R side). The results are shown in Table III. The transport rate decreased with increasing temperature. These membranes have a tendency to increase the ratio of initial transport rate between alkali metal ions (K<sup>+</sup>/Li<sup>+</sup>) with increasing temperature except the case of the membrane dried at 40°C. This means that the transport selectivity between alkali metal ions increased with increasing temperature. The maximum transport fraction was hardly changed by the temperature at which the membranes were dried. The swelling ratio and cation exchange capacity of the membranes dried at various temperatures were measured (Table IV). The swelling ratio decreased with increasing temperature. This indicates that the crosslinking was brought about by heating the membrane. Table IV also shows that the cation exchange capacity increased with increasing temperature. In the previous article,<sup>1</sup> we have reported that the increase of the cation exchange capacity with increasing UV irradiation time is attributed to the SH groups which were formed in the side reaction of the photocrosslinking of the poly(ETMA) membrane by UV irradiation.<sup>5</sup> The membranes dried at 50°C showed almost the same IR spectra as that of the membranes UV-irradiated. These facts indicate that the same crosslinking reaction occurred by both UV irradiation and drying of the membranes.

#### Selective Transport of Alkali Metal and Alkali Earth Metal Ions through the Membrane

Selective transport of Li<sup>+</sup> and Ca<sup>2+</sup> through the E7.5P2.5 membrane was investigated by using the system containing HCl solution (L side) and 0.025

TABLE IV  
Properties of ETMA-MP (7.5/2.5) Copolymer Membranes Dried at Various Temperatures

Membrane	Temp (°C)	Swelling ratio <sup>a</sup>	Cation exchange capacity (meq/g)
E7.5P2.5	30	1.81	1.90
	40	1.63	2.09
	50	1.53	2.12
	60	1.32	2.35

<sup>a</sup> Volume of wet resin in 0.1 mol dm<sup>-3</sup> KOH solution/volume of dry resin.

mol dm<sup>-3</sup> LiOH-0.025 mol dm<sup>-3</sup> CaCl<sub>2</sub> (R side). The results are shown in Figure 6. The HCl concentration in the L side was changed from 0.01 to 0.5 mol dm<sup>-3</sup>. In all cases, Ca<sup>2+</sup> was transported more rapidly than Li<sup>+</sup>. Ca<sup>2+</sup> was transported from the R side to the L side against its concentration gradient after 2 h, when above 0.05 mol dm<sup>-3</sup> HCl was used in the L side. The maximum transport rate and transport fraction were obtained when 0.1 mol dm<sup>-3</sup> HCl was used. In the case of 0.01 mol dm<sup>-3</sup> HCl, pH in both sides became alkaline, whereas, in other cases, it became acidic within 5 h.

The selective transport between Li<sup>+</sup> and Ca<sup>2+</sup> through the E7.5P2.5 membrane was also investigated by using the system containing HCl (0.05, 0.1, 0.25, 0.5 mol dm<sup>-3</sup>) solution in the L side and 0.05 mol dm<sup>-3</sup> LiCl-0.05 mol dm<sup>-3</sup> CaCl<sub>2</sub> in the R side (Fig. 7).

Ca<sup>2+</sup> was transported more rapidly than Li<sup>+</sup> through the membrane and Ca<sup>2+</sup> was transported against its concentration gradient from the R side to the L side after about 18 h when 0.25 mol dm<sup>-3</sup> HCl solution was used in the L side, although the transport rate of those metal ions was smaller than that in the system containing LiOH in the R side. We have reported that Li<sup>+</sup> was not transported through the ETMA-methacrylic acid copolymer membrane by using the system containing HCl (L side) and LiCl (R side).<sup>1</sup> The pH change of both sides was also measured (Fig. 8). In all cases, the pH of both sides became acidic. The small transport rate is attributed to the small pH difference between the L side and the R side as shown in Figure 8. Thus the transport of alkali or alkali earth metal ion through the ETMA-MP copolymer membranes was found to be greatly affected by the difference of H<sup>+</sup> concentration in both sides. How-

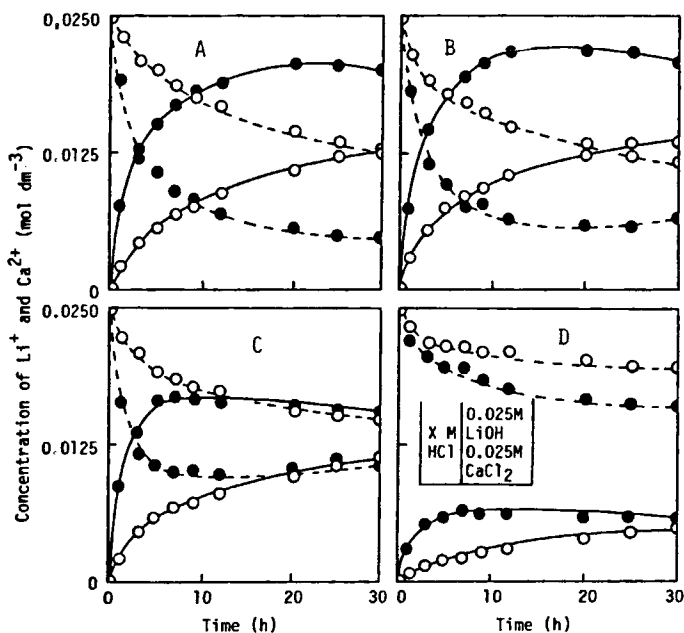


Fig. 6. Changes in concentration of Li<sup>+</sup> and Ca<sup>2+</sup> on the two sides of the membranes. E7.5P2.5: (—) L side; (---) R side; (○) Li<sup>+</sup>; (●) Ca<sup>2+</sup>. Initial HCl concentration in the L side (mol dm<sup>-3</sup>): (A) 0.5; (B) 0.1; (C) 0.05; (D) 0.01.

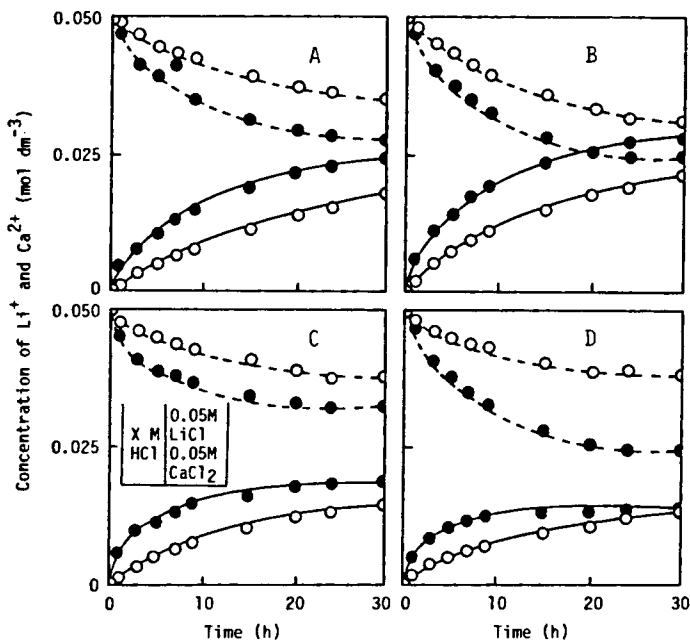


Fig. 7. Changes in concentration of  $\text{Li}^+$  and  $\text{Ca}^{2+}$  on the two sides of the membranes. E7.5P2.5: (—) L side; (---) R side: (○)  $\text{Li}^+$ ; (●)  $\text{Ca}^{2+}$ . Initial HCl concentration in the L side ( $\text{mol dm}^{-3}$ ): (A) 0.5; (B) 0.25; (C) 0.1; (D) 0.05.

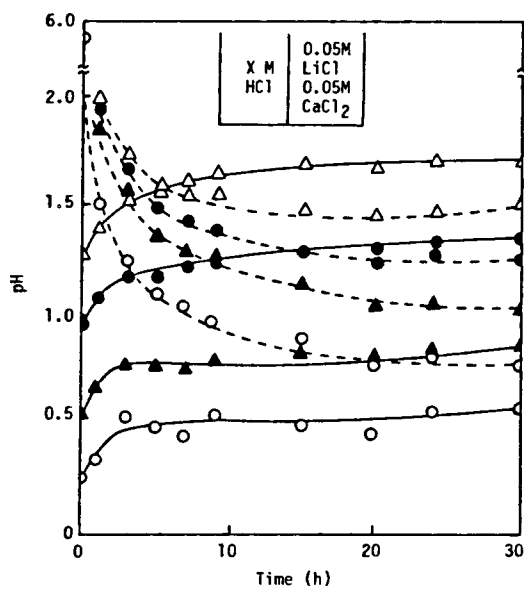


Fig. 8. Changes of pH on both sides: Membrane, E7.5P2.5: (—) L side; (---) R side. Initial HCl concentration in the L side ( $\text{mol dm}^{-3}$ ): (○): 0.5; (▲): 0.25; (●): 0.1; (△): 0.05.

ever, the exact mechanism of transport of alkali or alkali earth metal ions through the ETMA-MP copolymer membranes is not clear at present. It was also found that the pH of the R side became smaller than L side after 5 and 15 h when 0.05 and 0.1 mol dm<sup>-3</sup> HCl were used in the L side, respectively. This indicates that H<sup>+</sup> was transported against concentration gradient from the L side to R side.

### CONCLUSION

ETMA-MP copolymer membranes were prepared by evaporation of solvent from the DMF polymer solution at the desired temperature (mainly at 50°C). ETMA-MP copolymer membranes transported alkali metal and alkali earth metal ion more rapidly against their concentration gradient than ETMA-MAC copolymer membranes and the maximum transport fraction was more than 95%. The transport rate and transport fraction were affected by H<sup>+</sup> concentration in the L side. The effect of UV irradiation on the transport rate and the transport fraction was small. Ca<sup>2+</sup> was transported more rapidly than Li<sup>+</sup> against its concentration gradient in the system containing above 0.05 mol dm<sup>-3</sup> HCl in the L side and 0.025 mol dm<sup>-3</sup> LiOH-0.025 mol dm<sup>-3</sup> CaCl<sub>2</sub> in the R side.

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