

Effect of Ultraviolet Irradiation on the Selective Transport of Alkali Metal Ions through 2,3-Epithiopropyl Methacrylate–Methacrylic Acid Copolymer Membrane

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Synopsis

Cationic exchange membranes were prepared with 2,3-epithiopropyl methacrylate (ETMA)–methacrylic acid (MAc) copolymer. Transport of alkali metal ions against their concentration gradient through the membranes was investigated by using the system which contains HCl (left side) and alkali metal solution including two kinds of alkali hydroxides (right side). The effect of ultraviolet (UV) irradiation on the selective transport of alkali metal ions through the ETMA–MAc copolymer membranes was investigated. The membranes were irradiated with a 6-W low pressure mercury lamp at a distance of 10 cm at room temperature in air. The transport selectivity could be increased by using UV-irradiated 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. The maximum selectivity of K^+/Na^+ , Na^+/Li^+ , and K^+/Li^+ were 1.7, 2.0, and 4.2, respectively. In order to explain this phenomena, the effect of UV irradiation on the properties of the membranes was studied. It was concluded that the increase of the selectivity is attributed to the formation of the dense membrane by photocrosslinking of the membrane by UV irradiation.

INTRODUCTION

In the previous paper,¹ we have reported that Li^+ could be transported against its concentration gradient through the membranes made of ETMA–MAc copolymer, the membranes could be strengthened by photocrosslinking by UV irradiation, and the transport rate and transport fraction depended considerably on the compositions of the membrane. Furthermore, the transport fraction of Li^+ could be increased by using the copolymer membranes irradiated with UV light, because the physical and chemical structure of the membrane made of ETMA–MAc copolymer can be changed by irradiation of UV light of 254 nm.

This report is concerned with the effect of irradiation of UV light on the selective transport of alkali metal ions through the ETMA–MAc copolymer membranes.

EXPERIMENTAL

Synthesis of ETMA-MAC Copolymer

ETMA was prepared by the method reported earlier.² ETMA-MAC copolymers with various MAC contents were prepared by a solution polymerization 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 reprecipitating from the 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 the flask combustion method.³

Preparation Method of Membrane

The membranes were made by pouring the 5% copolymer dioxane solution onto a glass plate (5 × 5 cm), and allowing evaporation of the solvent at room temperature for 12 h. The membranes prepared were removed from the glass plate in water. 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 desired time in air. The 6-W low pressure mercury lamp (27 × 15 mm φ) (Ushio OLO 6AB6) was used as a light source for the photocrosslinking of the copolymers. The thickness of the membrane was 20–25 μm.

Apparatus and Measurement

Transport experiments were 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⁻ in both cells was determined by the Fajans method.⁴ 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 shaken 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 dm⁻³ 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 Adsorption Selectivity for Alkali Metal Ions by Batch Method

The dried membrane (0.25 g) was placed in a 100 cm⁻³ Erlenmeyer flask. Then 30 cm³ of 0.1 mol dm⁻³ alkali metal solution containing two kinds of alkali metal ions was poured into the flask. The mixture was allowed to stand at 30°C for 96 h with shaking. The adsorption selectivity for metal ions was determined by measuring the concentration of each residual metal ion in the supernatant by flame emission spectroscopy. The adsorption selectivity was calculated as follows:

$$\text{adsorption selectivity } (M_1^+/M_2^+) = \frac{M_1^+ \text{ adsorbed (meq/g)}}{M_2^+ \text{ adsorbed (meq/g)}} \quad (2)$$

where M_1^+ and M_2^+ are alkali metal ions investigated.

Measurement of the Swelling Ratio of the Membrane

The membrane was immersed in a 0.1 mol dm⁻³ KOH solution for 24 h and the swelling ratio of the membrane was calculated as follows:

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

where v and v' represent the volume of dry and wet membranes, respectively. The v and v' were measured by the method reported earlier.¹

RESULTS AND DISCUSSION

Synthesis of ETMA-MAC Copolymers with Various MAC Contents

Two kinds of ETMA-MAC copolymers with different compositions were synthesized for this research and they 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.

Selective Transport of Alkali Metal Ions through the ETMA-MAC Copolymer Membrane

In the previous article,¹ we have reported that Li⁺ was transported against its concentration gradient through the ETMA-MAC copolymer membranes

TABLE I
ETMA-MAC Copolymers Used for This Research

Abbreviation of membranes	Feed		1,4-dioxane (cm ³)	ETMA-MAC in copolymer (mol ratio)
	ETMA (cm ³)	MAC (cm ³)		
E7M3	7.0	3.0	20	43.7/56.3
E8M2	8.0	2.0	20	52.4/47.6

and that the copolymer membranes with high MAc content could also be used without breaking by irradiation of UV light and the transport fraction of Li^+ could be increased by using the E8M2 or E7M3 copolymer membrane irradiated with UV light.

The transport fraction and transport rate were defined as follows:

$$\text{transport fraction (\%)} = \frac{C_{\max}}{C_0} \times 100 \quad (4)$$

where C_0 is the initial concentration of alkali metal ion in the R side and C_{\max} is the maximum concentration of alkali metal ion in the L side.

$$\text{transport rate (mol h}^{-1} \text{cm}^{-2}) = \frac{m_t}{t \times s} \quad (5)$$

where m_t , t , and s are the amount (mol) of alkali metal ion in the L side after t hours at the initial stage, the transport time (h), and the effective membrane area (cm^2), respectively.

The increase of the transport fraction is due to the photocrosslinking of the membrane *in situ* and, consequently, the backtransfer of transported Li^+ from the L side to R side caused by the concentration gradient being depressed.

The effect of UV irradiation on the selective transport of alkali metal ions was investigated by using the M8M2 membrane UV-irradiated for various times. The results are shown in Figures 1–3. The L side was 0.1 mol dm^{-3} HCl solution and the R side was aqueous solution containing two kinds of alkali hydroxides (NaOH/LiOH, KOH/NaOH, and KOH/LiOH). The initial concentration of each alkali metal ion in the R side is 0.05 mol dm^{-3} . In the case of the membrane nonirradiated, the concentration of alkali metal ions in both sides became almost the same after about 20 h, although a certain alkali metal ion was found to be transported slightly at first against its concentration gradient. In the case of the membranes irradiated with UV light, the large difference of transport rate of each ion was observed. The transport rate decreased with increasing time of irradiation for all the systems; therefore, it

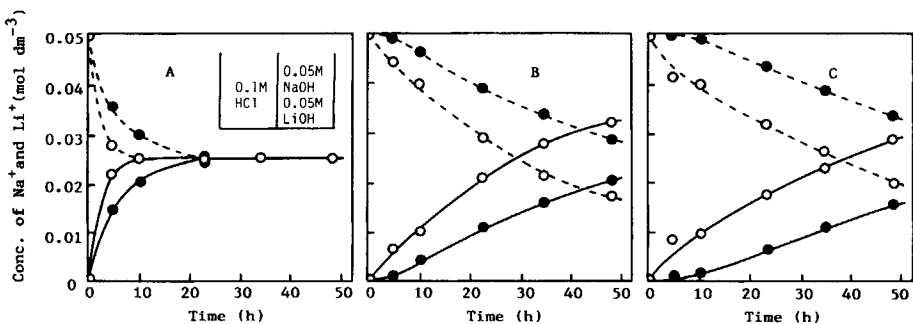


Fig. 1. Changes in concentration of Na^+ and Li^+ on the two sides of the membrane E8M2: (○) Na^+ ; (●) Li^+ ; (—) L side; (---) R side. UV-irradiated time (h): (A) 0; (B) 1; (C) 3. $0.1M$ HCl; $0.05M$ NaOH; $0.05M$ LiOH.

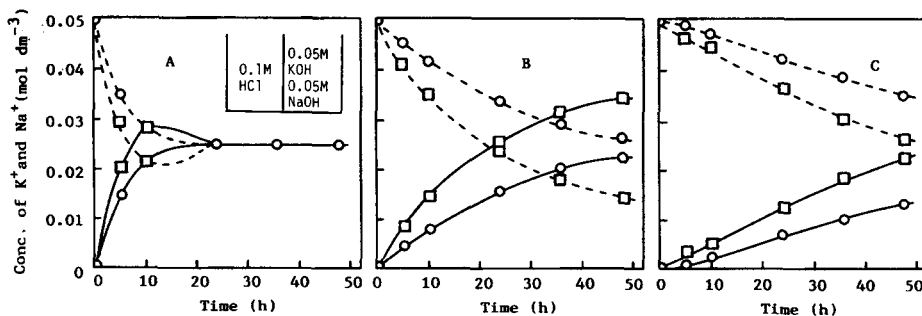


Fig. 2. Changes in concentration on K^+ and Na^+ on the two sides of the membrane E8M2: (\square) K^+ ; (\circ) Na^+ ; (—) L side; (---) R side. UV-irradiated time (h): (A) 0; (B) 1; (C) 3. 0.1M HCl; 0.05M KOH; 0.05M NaOH.

took a long time for each alkali metal ion in the L side to reach the maximum concentration. In most cases, after the concentration of alkali metal ions in the L side reaches maximum, it decreases gradually with time because of backtransfer of transported alkali metal ions by the concentration gradient. In this experiment, the change of concentration of alkali metal ions was measured up to 50 h to compare the transport selectivity of alkali metal ions. The transport selectivity of alkali metal ions through the membranes was plotted as a function of irradiation time (Fig. 4). The transport selectivity of the alkali metal ions through the membrane was calculated from the following equation:

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

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 M_{10}^+ and M_{20}^+ are the initial concentrations of each alkali metal ion in the R side. The highest selectivity of Na^+/Li^+ and K^+/Li^+ was obtained with the membrane irradiated for 2 h, while the highest selectivity of K^+/Na^+ was obtained with the membrane irradiated for 1 h. The maximum values of K^+/Na^+ , Na^+/Li^+ ,

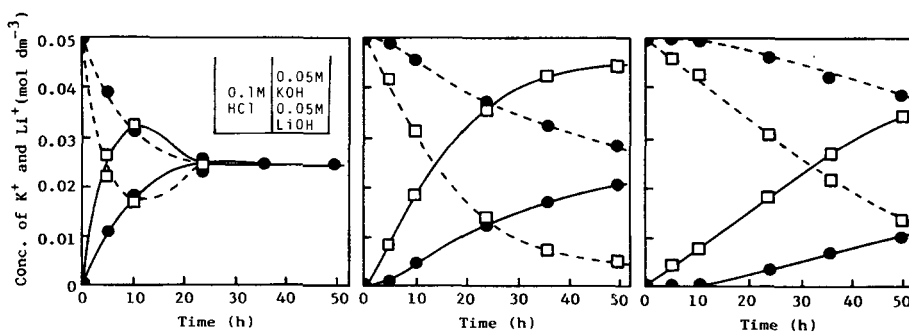


Fig. 3. Changes in concentration of K^+ and Li^+ on the two sides of the membrane E8M2: (\square) K^+ ; (\bullet) Li^+ ; (—) L side; (---) R side. UV-irradiated time (h): (A) 0; (B) 1; (C) 3. 0.1M HCl; 0.05M KOH; 0.05M NaOH.

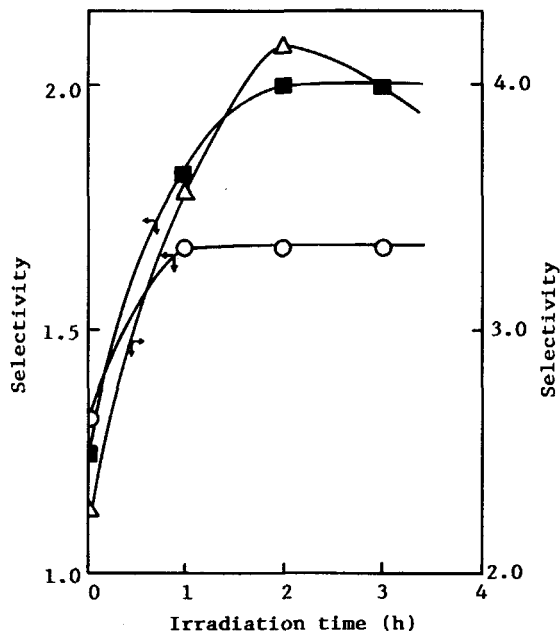
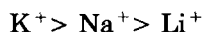


Fig. 4. Effect of UV irradiation on the selectivity in the transport of alkali metal ions; membrane, E8M2: (■) Na⁺/Li⁺; (Δ) K⁺/Li⁺; (○) K⁺/Na⁺.

and K⁺/Li⁺ were 1.7, 2.0, and 4.2, respectively. Thus the transport selectivity for alkali metal ions could be increased by using the membrane irradiated with UV light.

These results also indicate that the transport rate of alkali metal ions from the alkaline side to the acidic side through the membrane is given in the following order:



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:



Accordingly, the order of transport rate is inversely proportional to the size of the hydrated ions.

The effect of UV irradiation on the transport selectivity of alkali metal ions was also investigated by using the E7M3 membrane. However, the obvious tendency of the increase of transport selectivity with increasing time of UV irradiation was not observed because the E7M3 membrane transported all alkali metal ions pretty faster than the E8M2 membrane.

Effect of UV Irradiation on the Properties of the ETMA-MAc Copolymer Membranes

The effect of UV irradiation on the properties of the ETMA-MAc copolymer membranes was investigated by using E8M2 and E7M3 membranes.

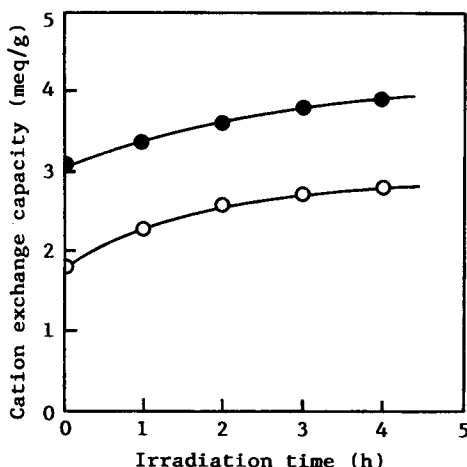


Fig. 5. Effect of UV irradiation on the cation exchange capacity. Membrane: (●) E7M3; (○) E8M2.

We have reported that SH groups could be formed in the side reaction of the photocrosslinking of PETMA and its copolymer by UV irradiation.⁵ It is known that SH groups behave as a weak acid, especially in alkaline solution.⁶ So the effect of UV irradiation on the cation exchange capacity of the membranes was first measured (Fig. 5). The cation exchange capacity increased slightly with increasing time of UV irradiation of the ETMA-MAc copolymer membranes.

The adsorption selectivity of the membranes which showed the increase in cation exchange capacity with time by UV irradiation was measured for the K^+/Li^+ , Na^+/Li^+ , and K^+/Na^+ systems by a batch method described in Experimental.

The dependence of selectivity (K^+/Li^+) on the UV irradiation time is shown only for E8M2 in Figure 6. The K^+/Li^+ values decreased with increasing time of UV irradiation, and all the values obtained with the membrane irradiated for various times were 1.38–1. The reason for this decrease of selectivity with increasing time of UV irradiation is not clear. The values of Na^+/Li^+ and K^+/Na^+ had also a tendency to decrease with increasing time of UV irradiation, and they were almost the same as the K^+/Li^+ values. The results indicate that the adsorption order of this membrane for alkali metal ions was $K^+ > Na^+ > Li^+$ and UV irradiation did not increase the adsorption selectivity for alkali metal ions, while it increased the cation exchange capacity of the membranes with increasing irradiation time.

Next the effect of UV irradiation on the swelling ratio was investigated for E8M2 and E7M3 membranes (Fig. 7). The swelling ratio of the E7M3 membranes is higher than that of the E8M2 membranes and the swelling ratio of both membranes decreased with increasing time of UV irradiation. The increase of swelling ratio by increased cation exchange capacity due to SH groups was not observed. The decrease of swelling ratio is attributed to the increased photocrosslinking of the membrane by UV irradiation.

The decrease of transport rate of alkali metal ions through the ETMA-MAc copolymer membranes irradiated with UV light indicates that hydrated alkali

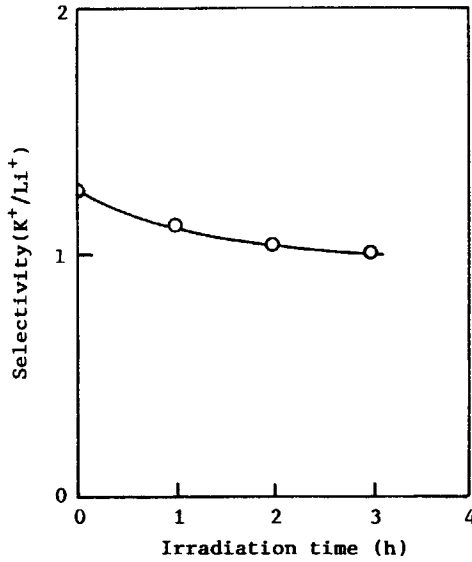


Fig. 6. Effect of UV irradiation on the selective adsorption of alkali metal ions by a batch method; membrane, E8M2.

metal ions become difficult to permeate through the irradiated membrane because the membrane becomes dense by the photocrosslinking of the membrane by UV irradiation. Furthermore, it is considered that the transport of larger hydrated ion becomes more difficult to permeate through the irradiated membrane than the smaller hydrated ions, so that the selectivity of K⁺/Li⁺, Na⁺/Li⁺, and K⁺/Na⁺ increased with increasing time of UV irradiation, while the transport rate of each alkali metal ion decreased with increasing time of UV irradiation. These results indicate that the transport selectivity was not only affected by the affinity between metal ions and carrier such as carboxyl groups but also by the microstructure of the wet membranes.

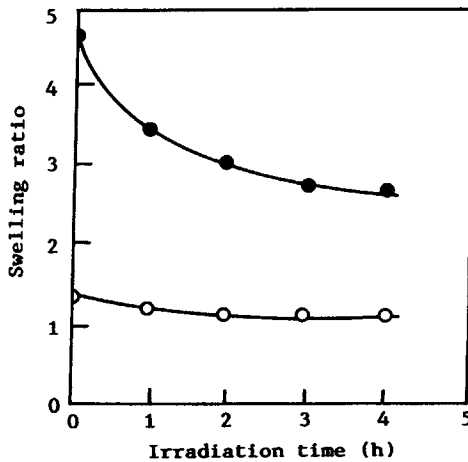


Fig. 7. Effect of UV irradiation on the swelling ratio. Membrane: (●) E7M3; (○) E8M2.

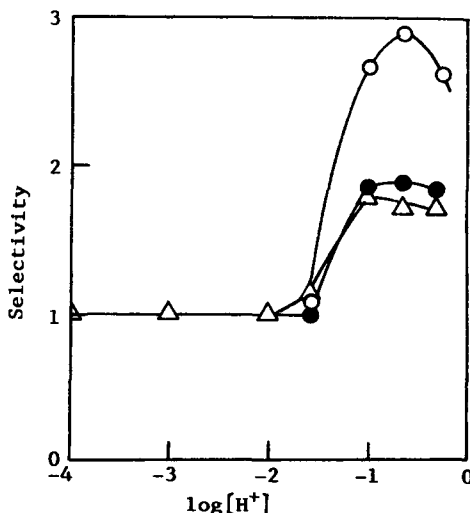


Fig. 8. Effect of the initial concentration of H^+ in the L side on the selectivity in the transport of alkali metal ions: membrane, E8M2 UV-irradiated for 1 h: (Δ) Na^+/Li^+ ; (\circ) K^+/Li^+ ; (\bullet) K^+/Na^+ .

Effect of pH on the Selective Transport

The transport selectivity was also measured by varying pH in the L side (Fig. 8). The initial concentration of each alkali metal ion in the R side was kept constant at 0.05 mol dm^{-3} and that of hydrochloric acid in the L side was changed. The selectivity was calculated by measuring the concentration of each ion in the L side after 24 h. In all systems, the maximum selectivity was obtained at pH 0.65–1.0, and the selectivity decreased rapidly with increasing pH above one until it became constant at unity at pH higher than 1.5. In the case of initial pH above 1.5, the solutions on both sides became alkaline after several hours during the transport of alkali metal ions, because the initial concentration of alkali hydroxide in the R side is higher than that of hydrochloric acid in the L side. The selectivity of unity implies that each ion was transported at almost the same speed through the membrane. This is attributed to the fact that the membrane became highly swelled by the alkaline solution. On the other hand, in a lower pH region, a permeation resistance between hydrated each ion and the membrane occurred because the membrane having carboxyl groups became dense, and consequently the increase of selectivity was due to the difference of hydrated size of each ion.

CONCLUSION

From the results, it was found that the transport selectivity of alkali metal ions through the membrane can be increased by using the membrane irradiated by UV light. It is considered that photocrosslinking of the membrane by UV light is an efficient method to change delicately the microstructure of the membrane and consequently to give the high transport selectivity between alkali metal ion, although the transport rate of alkali metal ions through the membrane decreases.

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