Preparation and Properties of Monovalent Anion Permselective Anion Exchange Membranes

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In order to prepare a monovalent permselective anion exchange membrane, the surface of a precursor membrane, which was prepared from a membranous copolymer of chloromethylstyrene (CMS) and divinylbenzene (DVB) in the presence of poly(vinyl chloride), was treated with various amino compounds; the chloromethylphenyl groups in the membrane were then reacted with trimethylamine so as to introduce (trimethylammoniomethyl)phenyl groups. The anion exchange membranes which were modified with tetraethylenepentamine and 4-vinylpyridine showed a chloride anion permselectivity versus that of a sulfate one in electrodialysis. It was thought that the reaction between these amines and the chloromethylphenyl groups formed a higher crosslinking structure on the surface of the membrane.

Ion exchange membranes are used for many purposes: the electrodialytic concentration of seawater, the electrolysis of sodium chloride, the diffusion dialysis of acid solutions, and the demineralization of an aqueous salt solution. Especially, in the electrodialytic concentration of seawater, the monovalent ion permselectivity of the membrane relative to the polyvalent ions and the low electrical resistance of the membrane are important in order to save energy and to avoid scaling problems associated with precipitated materials, such as $CaSO_4 \cdot 2H_2O$, in the concentrated salt solution and the membranes.

The synthesis of monovalent anion permselective anion exchange membranes versus polyvalent ones has been reported.[1)] For example, a composite membrane in which a cation exchange membrane was laminated together with an anion exchange membrane showed a monovalent cation permselectivity relative to the polyvalent ions.[2)] An anion exchange membrane which was synthesized from a polycondensation product of *m*-phenylenediamine, phenol, and formaldehyde showed poor electrochemical properties, poor durability, and a permselectivity for monovalent anions over the polyvalent type.[3)] Moreover, an anion exchange membrane of the copolymerization type which contained polycondensation products of *m*-phenylenediamine and formaldehyde showed a permselectivity for monovalent anions over the polyvalent type.[4,5)] However, the membrane lost its initial monovalent anion permselectivity, because these polycondensation products gradually decomposed during the long-term electrodialytic concentration of seawater. Also, the permselectivity of the anion exchange membrane was remarkably changed by the adsorption of or ion exchange with an anionic surface-active agent, such as a polycondensation product of sodium naphthalenesulfonate and formaldehyde.[6,7)] However, the formation of an anionic polyelectrolyte layer on the surface of the anion exchange membrane increased the electrical resistance of the membrane, and displayed the characteristics of a bipolar membrane. Moreover, the monovalent anion permselectivity gradually decreased during the long-term electrodialysis of seawater with desorption of the anionic surfactant on the membrane surface. On the other hand, it was reported that the surface of the membrane was modified so as not to have quaternary ammonium groups in order to prepare a monovalent permselective anion exchange membrane;[8)] also, the effect of the hydrophobicity of the ion exchange groups of the anion exchange membranes on permselectivity between two anions was studied.[9)]

It was therefore desired that a stable permselective layer be bound to the matrix of the membrane surface by a covalent bond. Moreover, to avoid the characteristics of a bipolar membrane and an increase in the electrical resistance of the membrane, the permselective layer on the surface of the membrane should comprise a thin, dense crosslinked structure of a cationic polyelectrolyte. We tried to form a dense cationic polyelectrolyte layer comprising a crosslinked structure by reacting functional groups on the surface of the membrane with amino compounds. The precursor membrane, a membranous copolymer of CMS and DVB, was chosen because chloromethylphenyl groups are reactive. Tetraethylenepentamine and 4-vinylpyridine were selected to form a dense layer on the surface of the membrane. In this work, the preparation and electrochemical properties of the resultant anion exchange membranes with the permselective layer between monovalent and polyvalent anions were studied in detail.

Experimental

Material. Precursor Membrane. The precursor membranes were provided by Tokuyama Corporation. The precursor membranes for the anion exchange membrane were synthesized according to a "paste method",[10,11)] that is, copolymerization of chloromethylstyrene (CMS) and commercial divinylbenzene (com-DVB) in the presence of poly(vinyl chloride) powder using cloth as a support material. Com-DVB was a mixture of *m*-DVB (40.7%), *p*-DVB (16.7%), *m*, *p*-ethylvinylbenzene (39.9%), and *m*, *p*-diethybenzene (2.7%).[12] The membrane contained 8—15% of DVB/(CMS+com-DVB), and the membrane thickness was about 0.11 mm.

Reagents. Tetraethylenepentamine, 4-vinylpyridine, pyridine, trimethylamine (30% aqueous solution), methanol, acetone, sodium chloride, sodium sulfate, hydrochloric acid and aqueous ammonia, which were obtained from Wako Pure Chemical Industries Co., Ltd., were of reagent grade.

Reaction. Surface Modification of the Membrane. Chloromethylphenyl groups on the surface of the precursor membrane were reacted with various amines by immersing the membrane into various amine solutions at room temperature or elevated temperature. After the membranes had reacted with the amines, chloromethylphenyl groups in the inner part of the membrane were quaternized with a mixture of acetone (1 part), water (1 part), and a 30% aqueous trimethylamine solution (2 part) at room temperature for one day.[13] The membrane was washed with 1 M (1 M = 1 mol dm^{-3}) hydrochloric acid, pure water, and then equilibrated with an aqueous 0.5 M sodium chloride solution.

Measurements. The electrochemical properties of the resultant membranes, which had been modified with amines, that is, the electrical resistance, monovalent anion permselectivity, ion exchange capacity, water content, and fixed ion concentration of the exchange groups of the membranes were measured. The electrical resistance of the membranes was measured with a 1000-cycle AC signal at 25 °C in an aqueous 0.500 M sodium chloride solution.

The monovalent anion permselectivity was evaluated by measuring the relative transport number of sulfate ions relative to chloride ions. After the membrane was placed in a two-compartment cell, the cathode compartment was filled with a mixed salt solution comprising 0.250 M sodium chloride and 0.125 M sodium sulfate; the anode compartment was filled with a 0.500 M sodium chloride solution (the effective membrane area was 2 cm×5 cm). Electrodialysis was carried out at a current density of 20 mA cm^{-2} for 60 m at 25 °C with stirring at 1500±100 rpm using Ag–AgCl electrodes. The relative transport number of sulfate ions relative to chloride ions is defined as

$$P_{\mathrm{Cl}}^{\mathrm{SO4}} = (t_{\mathrm{SO4}}/t_{\mathrm{Cl}})/(C_{\mathrm{SO4}}/C_{\mathrm{Cl}}),$$

where t_{SO4} and t_{Cl} are the transport number of sulfate ions and chloride ions, respectively, in the membrane, and C_{SO4} and C_{Cl} are the concentration of sulfate ions and chloride ions, respectively, at the cathode compartment solution before electrodialysis. After electrodialysis, the sulfate ions in the anode compartment were analyzed by the chelate back-titration method using ethylenediaminetetraacetic acid and barium chloride. The ion exchange capacity of the membrane, water content, and fixed ion concentration of the ion exchange groups were measured by conventional methods. The membranes (5 cm×5 cm, 2 sheets) were equilibrated with 1 M hydrochloric acid, a 0.5 M ammonia solution, washed with pure water, a 0.5 M sodium chloride solution, and then washed completely with pure water. The membranes were then equilibrated in a 2 M sodium nitrate solution, and the released amount of chloride ions by the replacement of nitrate ions was measured by Mohr's method. The ion exchange capacity of the membrane equals the amount of chloride ion. The content of quaternized chloromethylphenyl groups which had been formed by the reaction between the chloromethylphenyl groups and 4-vinylpyridine in the precursor membrane was determined by measuring the amount of chloride ions, such as by a measurement of the anion exchange capacity.

The IR spectra were recorded by the ATR (attenuated total reflection) technique using a Perkin–Elmer 1600 FTIR spectrophotometer in order to confirm the presence of pyridinium groups on the surface of the membrane.

Results and Discussion

Relationship between the Content of DVB/(CMS+com-DVB) in the Membrane and the Electrochemical Properties of Membranes. First of all, before the formation of a highly crosslinked layer on the anion exchange membrane, the properties of the anion exchange membrane were examined based on its composition. It is well-known that the electrochemical properties of the membrane, that is, the ion exchange capacity, water content, and electrical resistance of the membrane depend on the content of DVB/(CMS+com-DVB). The ion exchange capacity and water content of the membranes decreased with an increase in the nominal DVB content in a membranous copolymer of CMS and com-DVB. The electrical resistance of the membrane also increased with an increase in the DVB content because of the decrease in the ion exchange capacity. It was reported that the concentration of fixed sulfonic acid groups in sulfonated styrene–divinylbenzene copolymers increased along with an increase in the degree of the nominal crosslinking.[14] Figure 1 shows that the concentration of the fixed (trimethylammoniomethyl)phenyl groups in the anion exchange membrane increased from 5 to 9 mol kg^{-1} along with an increase in the nominal DVB content.

The permselectivity of the polyvalent ion relative to the monovalent ion, that is, sulfate ion to chloride ion ($P_{\mathrm{Cl}}^{\mathrm{SO4}}$), decreased with an increase in the DVB content (Fig. 2). It was thought that the tighter the network of the membrane that was formed, more chloride ions relative to sulfate ions would permeate through the membrane in the electrodialysis.

Figure 3 shows the relationship between the concentration of fixed anion exchange groups in the membrane and the

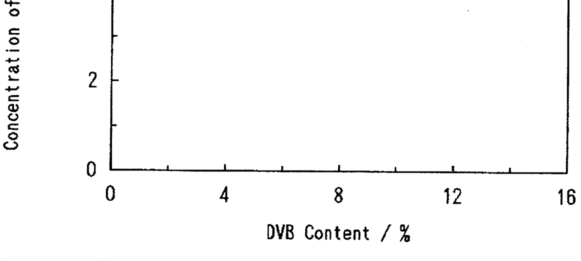

Fig. 1. Effect of nominal DVB content on concentration of fixed ion exchange groups.

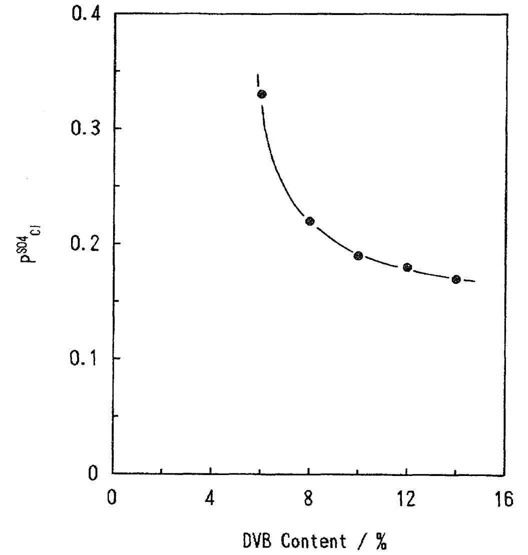

Fig. 2. Effect of nominal DVB content on permselectivity of P^{SO4}_{Cl}.

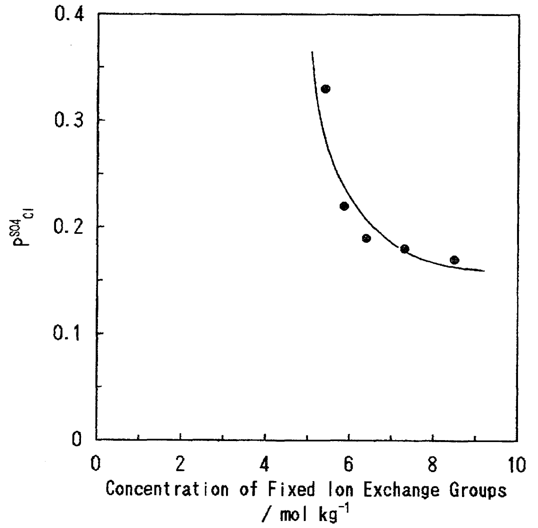

Fig. 3. Relationship between concentration of fixed ion exchange groups and P^{SO4}_{Cl}.

permselectivity of P^{SO4}_{Cl}. The permselectivity decreased with increasing concentration of the fixed anion exchange groups. It was thought that the decrease in free water in the membrane resulted in the transport of small hydrated ions rather than the large hydrated ions, that is, chloride ions rather than sulfate ions, because the size of the hydrated sulfate ion is larger than that of the chloride ion.

Formation of a Dense Crosslinking Structure by a Modification with Tetraethylenepentamine. In order to form a crosslinking structure on the surface of the membrane, chloromethylphenyl groups in the membrane were reacted with tetraethylenepentamine. The precursor membrane contained a nominal 15% DVB content in the membranous copolymer of CMS and com-DVB. At first, the precursor membrane was reacted with an aqueous 10% tetraethylenepentamine solution under reflux for 1—3 h, and was then reacted with a trimethylamine solution for one day. The increase in electrical resistance of the membranes was slight, and the permselectivity for sulfate ion relative to the chloride ion (P^{SO4}_{Cl}) was about 0.15—0.16. This value was almost the same (P^{SO4}_{Cl}) as that of an ordinal anion exchange membrane containing a nominal 15% DVB content. It seemed that the chloromethylphenyl groups on the surface of the membrane did not react with much of the tetraethylenepentamine.

In order to decrease the anion exchange groups on the membrane surface and depress swelling of the membrane, a trial to decompose chloromethyl groups to hydroxymethyl groups was carried out. The precursor membrane was first reacted with an aqueous 6% sodium hydroxide solution under reflux for 1—2 h and, then reacted with trimethylamine. The increase in electrical resistance of the membrane was slight and the permselectivity for the sulfate ion relative to the chloride ion (P^{SO4}_{Cl}) decreased slightly (Fig. 4). It seemed that the hydrophobic precursor membrane did not react with hydrophilic agents, such as the aqueous sodium hydroxide solution under these conditions. The ATR spectra of the surface of the treated membrane failed to show evidence of hydroxymethyl groups.

The precursor membrane was reacted with an aqueous mixture of 10% tetraethylenepentamine and 6% sodium hydroxide solution under reflux for 0.5—2 h. Chloromethylphenyl groups in the inner part of the membrane were then quaternized with the trimethylamine solution. In this case, the electrical resistance of the membrane increased with an increase in the reaction time. Moreover, the permselectivity for the sulfate ion relative to the chloride ion (P^{SO4}_{Cl}) decreased to 0.01. Therefore, the reaction between the chloromethylphenyl groups and tetraethylenepentamine took place on the surface of the membrane to form a dense crosslinking

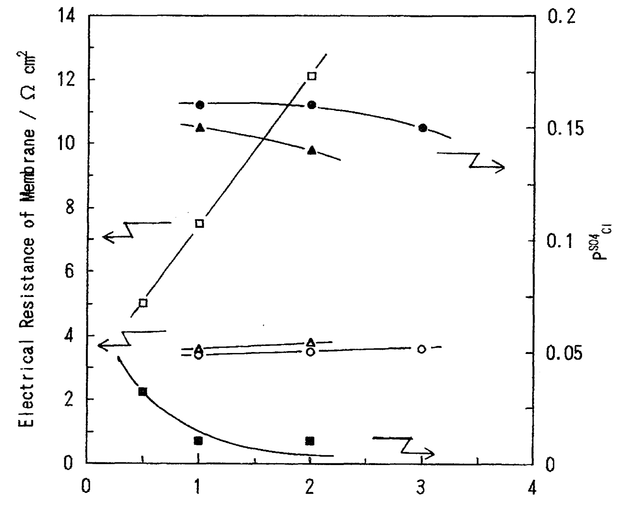

Fig. 4. Effect of reaction time of amine on electrical resistance of membrane (Ω cm^2) and P^{SO4}_{Cl} under reflux: Ω cm^2, P^{SO4}_{Cl} ○, ● an aqueous 10% tetraethylenepentamine solution; △, ▲ an aqueous 6% NaOH solution; □, ■ an aqueous mixture of 10% tetraethylenepentamine and 6% NaOH solution.

structure. It was found that sodium hydroxide was necessary to allow the reaction to proceed between chloromethylphenyl groups and tetraethylenepentamine on the surface of the membrane. Sodium hydroxide acted as a dehydrochlorination agent and a promoter of the reaction. However, no evidence for amino groups on the surface of the membrane was observed in the ATR spectrum, because the surface of the membrane became rough due to the high-temperature reaction. The nitrogen content of the precursor membrane, which was reacted with 10% tetraethylenepentamine and 6% sodium hydroxide solution, was determined by elemental analysis. Table 1 shows the ratio of the reacted tetraethylenepentamine/chloromethylphenyl groups of the precursor membrane (ion exchange capacity). Though these values were small, there were a few weakly basic amino groups which underwent crosslinking with the benzyl groups on both sides of the membrane. These layers displayed an effective monovalent anion permselectivity because they were thin and dense and had weakly cationic polyelectrolyte layers. It was thought that the water content in a weak cationic polyelectrolyte layer would be less than that in a strong cationic one. The chemical structure of the inner part of the membrane is shown in Fig. 5(a). Chloromethylphenyl groups in the membrane were reacted with trimethylamine to form (trimethylammoniomethyl)phenyl groups. On the other hand, on the surface of the membrane there were weak amino ion exchange groups which were reacted with tetraethylenepentamine and chloromethylphenyl groups, as shown in Fig. 5(b).

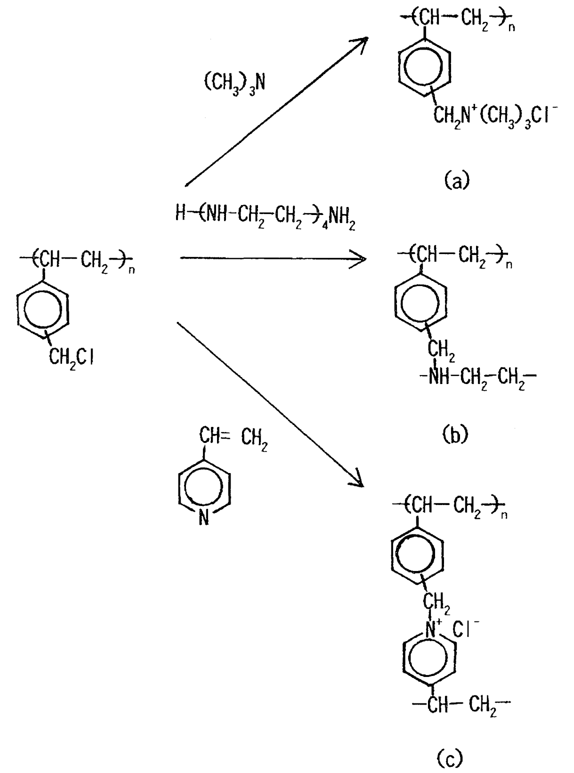

Fig. 5. Chemical structure of the membrane: (a) interior part of the membrane, (b) surface of the membrane reacted with tetraethylenepentamine, (c) surface of the membrane reacted with 4-vinylpyridine.

In the case of the reaction with an aqueous tetraethylenepentamine solution, the nitrogen content was too small to determine the existence of tetraethylenepentamine on the membrane.

Formation of a Dense Crosslinking Structure by Matrix Polymerization of 4-Vinylpyridine. The membrane which reacted with tetraethylenepentamine under reflux conditions showed an effective monovalent anion permselectivity. However, a mild reaction condition was desirable for preparing an anion exchange membrane. It was reported that 4-vinylpyridine took part in the matrix polymerization when 4-vinylpyridine was quaternized.[15] In order to form a dense crosslinking structure, the surface of the precursor membrane was reacted with a mixture of 20% 4-vinylpyridine and 80% methanol at room temperature for 6—48 h. The remaining chloromethylphenyl groups of the precursor membrane were then quaternized with the trimethylamine solution. Figure 6 shows the effect of the reaction time on the permselectivity for the sulfate ion relative to the chloride ion ($P_{\mathrm{Cl}}^{\mathrm{SO_4}}$) and the electrical resistance of the membrane. At the same time, Fig. 6 shows the permselectivity and electrical resistance of the membrane which was reacted with a 20% pyridine and 80% methanol solution at room temperature for 24—48 h. Though, the electrical resistance of the membrane which was reacted with pyridine slightly increased, the monovalent anion permselectivity was not improved because of a swelling of the membranous copolymer by pyridine. However, 4-vinylpyridine showed effective monovalent anion permselectivity and an increase in the electrical resistance of the membrane. Therefore, it was thought that a tight crosslinkage structure was developed by the quaternization and polymerization of 4-vinylpyridine on the surface of the membrane.

Figure 7 shows the ATR spectra of the precursor membrane modified by 4-vinylpyridine and pyridine, respectively. A characteristic peak was found at 1637 cm^{-1} which was attributed to quaternized 4-vinylpyridinium groups. Also, the quaternized pyridinium groups showed a characteristic peak at 1632 cm^{-1}. These peaks were thought to be the stretch-

Table 1. Amount of Reacted Tetraethylenepentamine on the Membrane

Reaction time h	Amino groups of reacted tetraethylenepentamine / Chloromethylphenyl groups (Ion exchange capacity) %
1	0.7
2	1.4

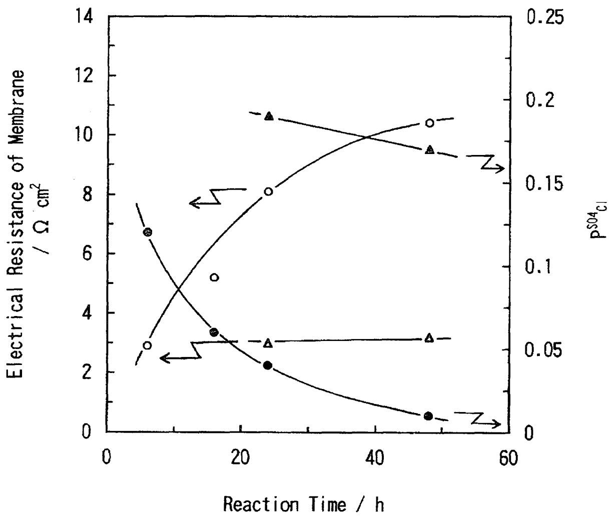

Fig. 6. Effect of reaction time of amine on electrical resistance of membrane (Ω cm^2) and $P_{\rm Cl}^{\rm SO4}$ at room temperature: Ω cm^2, $P_{\rm Cl}^{\rm SO4}$ ○, ● 20% 4-vinylpyridine and 80% methanol; △, ▲ 20% pyridine and 80% methanol.

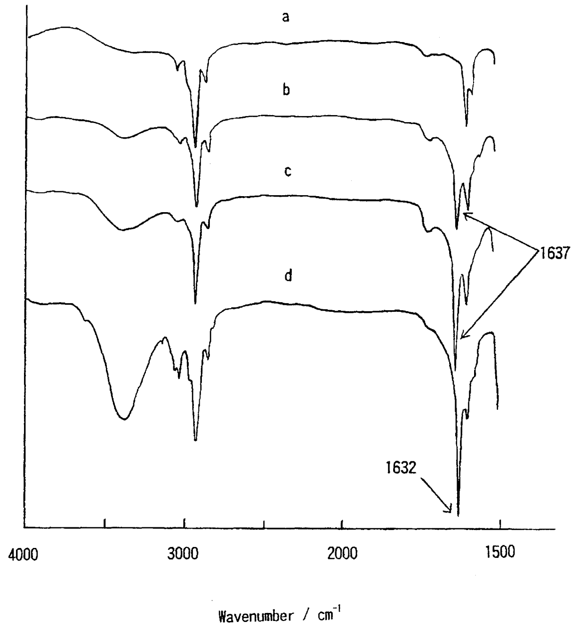

Fig. 7. ATR spectra of the membrane modified by amine at room temperature: (a) precursor membrane, (b) 20% 4-vinylpylidine and 80% methanol for 5 h, (c) 20% 4-vinylpylidine and 80% methanol for 24 h, (d) 20% pyridine and 80% methanol for 24 h.

ing vibration of C=C and C=N in the pyridine ring. The absorbance of 1637 cm^{-1} increased with an increment in the 4-vinylpyridine reaction time. The pendant vinyl groups in 4-vinylpyridine could not be assigned by the ATR.

Figure 8 shows the relationship between the ratio of quaternized 4-vinylpyridine by the chloromethylphenyl groups/ion exchange capacity (chloromethylphenyl groups of the precursor membrane) and the reaction time. The quaternized 4-vinylpyridinium groups were measured based on the content of chloride ions attached to the (pyridiniomethyl)phenyl groups. The increase in the reaction time resulted in an increase in the ratio of the quaternized 4-vinylpyridine groups/ion exchange capacity. Also, an elemental analysis of the nitrogen of the precursor membrane showed almost the same content as that of the chloride ions. Therefore, it was found that 4-vinylpyridine reacted with the chloromethylphenyl groups and the pendant vinyl groups of the quaternized 4-vinylpyridines copolymerized with neighbor quaternized 4-vinylpyridine, and did not copolymerize with free 4-vinylpyridine. On the surface of the membrane, dense crosslinking and strong cationic polyelectrolyte layers were formed. The chemical structure of the ion exchange groups on the surface of the membrane is shown in Fig. 5(c).

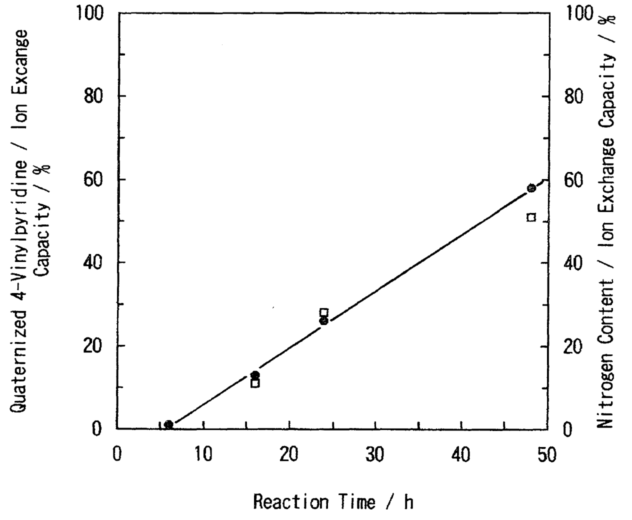

Fig. 8. Relationship between reacted amount of 4-vinylpyridine on the membrane and reaction time: ☐ quaternized amount of 4-vinylpyridine, ● nitrogen content of the precursor membrane.

However, the amination reaction seemed to proceed heterogeneously from the membrane surface because the membranous copolymer had an inhomogeneous crosslinking structure and a micro phase separation structure between the copolymer of CMS-DVB and poly(vinyl chloride) as a supporting substance.[12] Therefore, after trimethylamination of the membrane, it was thought that on the surface of the membrane there were poly[(4-vinylpyridiniomethyl)phenyl chloride] due to the copolymerization of pendant vinyl groups and a small amount of (trimethylammoniomethyl)phenyl groups. Though the remaining chloromethylphenyl groups did not form a crosslinking structure, most of the reacted 4-vinylpyridine formed a dense crosslinking and strong cationic polyelectrolyte structure by copolymerization of pendant vinyl groups. Therefore, the thick quaternized 4-vinylpyridine layer resulted in an effective monovalent anion permselective anion exchange membrane.

Conclusions. 1. A monovalent anion permselective membrane was obtained from a reaction with chloromethylphenyl groups and tetraethylenepentamine. A thin crosslinking structure comprising weak amino groups was formed on the surface of the membrane. 2. A membrane which was reacted with 4-vinylpyridine exhibited an effective monovalent permselectivity, though the membrane which was modified by pyridine showed a low monovalent permselectivity. When 4-vinylpyridines were quaternized with chloromethylphenyl groups, they were polymerized on the matrix of the membranous copolymer and then formed a dense crosslinking and strong cationic polyelectrolyte structure on the surface of the membrane.

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