

# Anion Exchange Membranes Prepared from Chloromethylstyrene and 2-Methyl-5-vinylpyridine

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## Synopsis

Strongly basic anion exchange membranes were prepared by the radical copolymerization of chloromethylstyrene and 2-methyl-5-vinylpyridine. The formation of a three-dimensional structure and the presence of the quarternary pyridinium group were confirmed by infrared spectrum analysis and its strongly basic anion exchange properties. Their electrochemical properties and morphology were compared with those of the anion exchange membranes prepared from chloromethylstyrene-divinylbenzene and 2-methyl-5-vinylpyridine-divinylbenzene. The chloromethylstyrene-2-methyl-5-vinylpyridine membranes were proved to have larger anion exchange capacity, smaller electric resistance, larger water content, and higher permeability than the chloromethylstyrene-divinylbenzene and 2-methyl-5-vinylpyridine-divinylbenzene membranes. Also, the membranes have heterogeneity in the cross-linking structure.

## INTRODUCTION

It is well known that the cross-linking degree of ion exchange membranes is one of the most effective factors to its properties: for example, the increase in the cross-linking degree increases electric resistance and decreases ion exchange capacity and water content.

The purpose of this study is to prepare anion exchange membrane with small electric resistance and high cross-linking degree by copolymerizing chloromethylstyrene (CMS) and 2-methyl-5-vinylpyridine (2M5VP). CMS and 2M5VP were copolymerized by using benzoylperoxide (BPO), thus, insoluble polymer containing quarternary pyridinium group can be obtained.<sup>1</sup> It can be considered that spontaneous copolymerization of CMS with vinylpyridines, of which the mechanism is analogous to the anion polymerization of the Kabanov type, might give a cross-linked copolymer containing quarternary pyridinium group and yield strongly basic anion exchange resin with good physicochemical properties.<sup>2-5</sup>

The preparation and properties of anion exchange membranes, which are copolymers of 4-vinylpyridine (4VP) and CMS, were investigated as efficient separators in a redox power storage cell system.<sup>6</sup> Here, the use of 2-vinylpyridine (2VP), 4VP, and 2M5VP were preliminarily tested, but the preparation of anion exchange membrane by molding copolymerization in the shape of the membrane was difficult in the cases of 2VP and 4VP, because their spontaneous polymerization rate was too rapid.<sup>7,8</sup> The spontaneous polymerization rate of 2M5VP was slower than those of 2VP and 4VP,<sup>9</sup> and therefore the

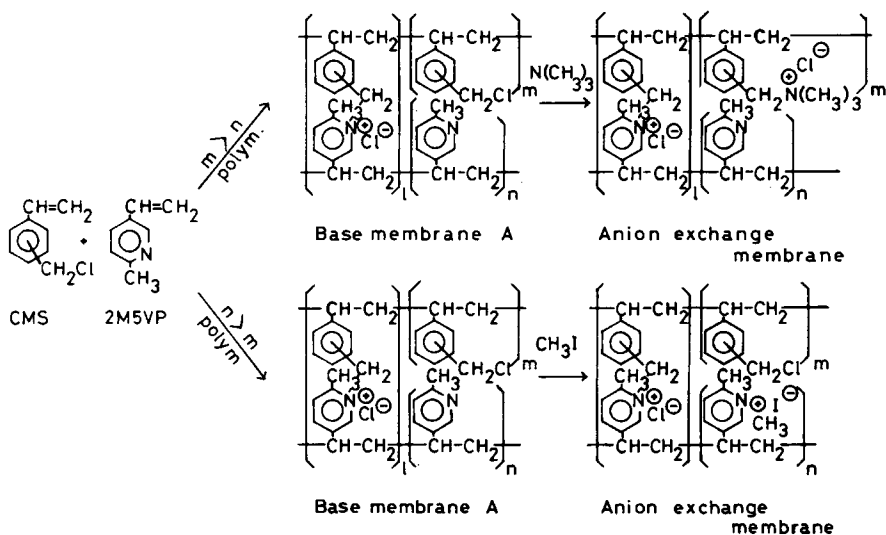


Fig. 1. Preparation route of CMS-2M5VP membranes.

membrane could be prepared only in the case of 2M5VP. Membrane properties were compared with those of the anion exchange membranes prepared from CMS-divinylbenzene (DVB) and 2M5VP-DVB.

## EXPERIMENTAL

### Materials

All materials used were of commercial grade. The CMS (Seimi Chemical Co., Ltd.) used was a mixture of dichloromethylstyrene (0.9%),  $\alpha$ -chloromethylstyrene (6.5%), *m*- and *p*-CMS (92.7%) and the purity of 2M5VP (Phillips Petroleum Co.) was 99.6%. The DVB used was a mixture of *m*- and *p*-diethylbenzene (2.7%), *m*- and *p*-ethylstyrene (39.9%), and *m*- and *p*-DVB (57.4%).

### Preparation of the Membranes

All membranes were prepared similarly to the paste method.<sup>10,11</sup> The preparation procedures are shown in Figures 1 and 2. Quarternization ratio of all the membranes treated with  $\text{N}(\text{CH}_3)_3$  or  $\text{CH}_3\text{I}$  was  $> 99\%$ .

**CMS-2M5VP Membrane:** A mixture consisting of CMS, 2M5VP, acrylonitrile-butadiene rubber (NBR), and  $\alpha, \alpha'$ -azo-bis-iso-butyronitrile (AIBN) was coated onto a polyvinylchloride (PVC) cloth (Teijin Limited) as a reinforcing material and then was heated at  $75^\circ\text{C}$  for 5 h under nitrogen atmosphere to copolymerize the monomers. Thus, the base membrane A was obtained. When the  $2\text{M5VP}/(\text{CMS} + 2\text{M5VP}) = 21.6\text{--}49.1$  mol%, the base membrane A contains mainly the quarternary pyridinium group and the surplus CMS unit, and the CMS unit is aminated with a mixed solution of  $\text{N}(\text{CH}_3)_3$ -acetone-water ( $\text{N}(\text{CH}_3)_3$ , 2.5 *N* and the volume ratio of acetone/water = 1/3) at  $30^\circ\text{C}$  for 16 h to affix the quarternary ammonium chloride groups. When the  $2\text{M5VP}/(\text{CMS} + 2\text{M5VP}) = 58.2\text{--}93.2$  mol%, the base membrane A was treated with a hexane solution of  $\text{CH}_3\text{I}$  (30 wt%) at

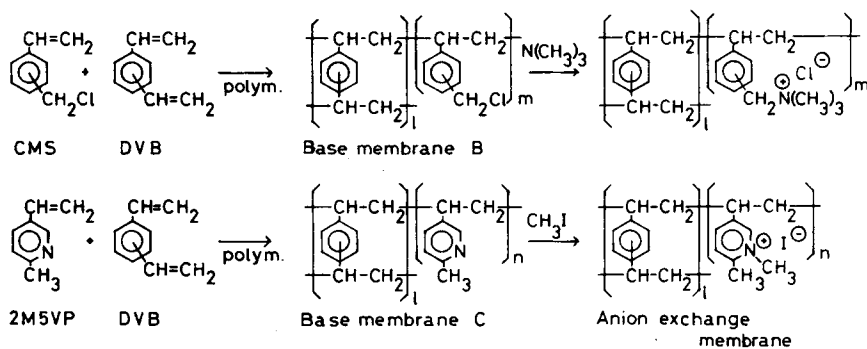


Fig. 2. Preparation route of CMS-DVB, 2M5VP-DVB membranes.

TABLE I  
Recipe for the CMS-2M5VP Membranes

No.	2M5VP		NBR		AIBN	
	CMS + 2M5VP (mol/mol)		CMS + 2M5VP (wt%)		CMS + 2M5VP (wt%)	
CM-1	$2.16 \times 10^{-1}$		3		1.5	
CM-2	$2.93 \times 10^{-1}$		3		1.5	
CM-3	$3.56 \times 10^{-1}$		3		1.5	
CM-4	$4.08 \times 10^{-1}$		3		1.5	
CM-5	$4.53 \times 10^{-1}$		3		1.5	
CM-6	$4.91 \times 10^{-1}$		3		1.5	
CM-7	$5.80 \times 10^{-1}$		3		1.5	
CM-8	$6.33 \times 10^{-1}$		3		1.5	
CM-9	$6.98 \times 10^{-1}$		3		1.5	
CM-10	$7.34 \times 10^{-1}$		3		1.5	
CM-11	$7.75 \times 10^{-1}$		3		1.5	
CM-12	$8.21 \times 10^{-1}$		3		1.5	
CM-13	$8.74 \times 10^{-1}$		3		1.5	
CM-14	$9.32 \times 10^{-1}$		3		1.5	

30 °C for 20 h in order to quaternize the surplus 2M5VP unit. Table I shows the recipe of the monomer mixture.

**CMS-DVB Membrane:** A mixture consisting of CMS, DVB, NBR, and BPO was coated onto the PVC cloth and then was heated to copolymerize the monomers at 65 °C for 5 h under nitrogen atmosphere. The base membrane B

TABLE II  
Recipe for the CMS-DVB Membranes

No.	DVB		NBR		BPO	
	CMS + DVB (mol/mol)		CMS + DVB (wt%)		CMS + DVB (wt%)	
CD-1	$0.68 \times 10^{-1}$		5		3	
CD-2	$1.10 \times 10^{-1}$		5		3	
CD-3	$1.39 \times 10^{-1}$		5		3	
CD-4	$1.69 \times 10^{-1}$		5		3	
CD-5	$2.14 \times 10^{-1}$		5		3	
CD-6	$2.93 \times 10^{-1}$		5		3	
CD-7	$3.78 \times 10^{-1}$		5		3	

TABLE III  
 Recipe for the 2M5VP-DVB Membranes

No.	DVB	NBR	AIBN
	2M5VP + DVB (mol/mol)	2M5VP + DVB (wt%)	2M5VP + DVB (wt%)
MD-1	$0.40 \times 10^{-1}$	3	1.5
MD-2	$0.82 \times 10^{-1}$	3	1.5
MD-3	$1.28 \times 10^{-1}$	3	1.5
MD-4	$1.78 \times 10^{-1}$	3	1.5

thus prepared was aminated with a mixed solution of  $N(\text{CH}_3)_3$ -acetone-water at  $30^\circ\text{C}$  for 16 h. Table II shows the recipe of the monomer mixture.

**2M5VP-DVB Membrane:** A mixture consisting of 2M5VP, DVB, NBR, and AIBN was coated onto the PVC cloth and then was heated to copolymerize the monomers at  $65^\circ\text{C}$  for 5 h under nitrogen atmosphere. The base membrane C obtained was treated with a hexane solution of  $\text{CH}_3\text{I}$  (30 wt%) at  $30^\circ\text{C}$  for 20 h to quaternize the 2M5VP unit.

Table III shows the recipe of the monomer mixture.

### Measurement

The anion exchange membranes were equilibrated alternately and several times in a 1 *N* HCl aqueous solution and in a 0.5 *N*  $\text{NH}_4\text{OH}$  aqueous solution. Anion exchange capacity, water content, electric resistance, and apparent diffusion coefficient<sup>15</sup> of NaCl were measured by the ordinary methods, as reported in the previous papers.<sup>11-14</sup>

The membrane equilibrated in a 1 *N* HCl aqueous solution was washed successively with water and ethanol, and then was dipped in a 0.5 *N*  $\text{NaNO}_3$  aqueous solution. The liberated  $\text{Cl}^-$  was titrated by the Mohr method (M mEq).

Next, the membranes were washed with water and equilibrated in a 0.5 *N* NaCl aqueous solution, and the membrane surface was quickly wiped with filter paper and weighted with the aid of a weighting bottle ( $W_1$ g). The membrane was washed with water and dried at  $50^\circ\text{C}$  for 5 h under vacuum to attain the constant weight ( $W_2$ g).

The following equations were used.

$$\text{Anion exchange capacity (EC)} = M/W_2(\text{mEq/g dry membrane of Cl}^- \text{ form}) \quad (1)$$

$$\text{Water content (WC)} = (W_1 - W_2)/W_2(\text{g H}_2\text{O/g dry membrane of Cl}^- \text{ form}) \quad (2)$$

$$\text{Fixed ion concentration (FC)} = M/(W_1 - W_2) (\text{mEq/g H}_2\text{O}) \quad (3)$$

Electric resistance (R) was measured in a 0.5 *N* NaCl aqueous solution at  $25^\circ\text{C}$  with an alternating current of 1 kHz.

Apparent diffusion coefficient of NaCl ( $D_{\text{NaCl}}$ ) was measured as follows.

The membrane was placed in a two-compartment cell. As soon as each of the compartments was filled with 300 mL of a 4.0 *N* NaCl aqueous solution and 100 mL of water, respectively, the solution and water were stirred (1800 rpm) at 25°C for 3 h. The amount of NaCl diffused into water was intermittently determined.

$D_{\text{NaCl}}$  was calculated as follows.

$$D = \frac{\delta \cdot m}{\Delta C \cdot A \cdot t} \quad (4)$$

where  $D$  is the apparent diffusion coefficient;  $\delta$ , thickness of the membrane (cm);  $m$ , the diffused amount of NaCl into water (eq);  $t$ , time (s);  $A$ , the effective membrane area (cm<sup>2</sup>); and  $\Delta C$ , the difference in the NaCl concentration between the two compartments (eq/cm<sup>3</sup>).

An infrared spectrum was measured by using a spectrophotometer, IR-400 from Shimadzu Corporation.

The morphology of the membrane was observed by using a transmission electron microscope, JEM-200CX from JEOL Ltd. Ultrathin samples of the base membranes were prepared by using an ultramicrotome and stained by exposure to the vapor of aqueous osmium tetroxide solutions at room temperature for 2 days.

### Estimation of the Cross-linking Degree

The cross-linking degree ( $D_{\text{cross}}$ ) of the CMS-2M5VP membrane can be estimated by measuring the anion exchange capacities as follows.

The participation ratio of 2M5VP with the cross-linking ( $P_{2\text{M5VP}}$ ) is estimated by Eq. (5) in the case of the molar ratio of 2M5VP/(CMS + 2M5VP) < 0.5.

$$P_{2\text{M5VP}} = \frac{l}{l + n} = \frac{E}{E'} \quad (5)$$

where  $E$  is the amount of the quaternary pyridinium group in the cross-linking unit, estimated as the anion exchange capacity of the base membrane A equilibrated in a mixture of 0.05 *N* NaOH aqueous solution and 4 *N* NaCl aqueous solution; and  $E'$  is the anion exchange capacity after the base membrane A was treated with CH<sub>3</sub>I as described before.

The participation ratio of CMS with the cross-linking ( $P_{\text{CMS}}$ ) is estimated by Eq. (6) in the case of the molar ratio of 2M5VP/(CMS + 2M5VP) > 0.5.

$$P_{\text{CMS}} = \frac{l}{l + m} = \frac{E}{E''} \quad (6)$$

where  $E''$  is the anion exchange capacity after the base membrane A was treated with N(CH<sub>3</sub>)<sub>3</sub> as described before.

Also,  $D_{\text{cross}}$  of the CMS-2M5VP membrane is defined in Eq. (7).

$$D_{\text{cross}} = \frac{l}{2l + m + n} \quad (7)$$

$D_{\text{cross}}$  of the CMS-DVB and 2M5VP-DVB membranes are defined as the molar ratio of DVB/(CMS + DVB) and DVB/(2M5VP + DVB), respectively.

### RESULTS AND DISCUSSION

The basic membrane A is insoluble in water and has strongly basic anion exchange properties. These facts show the base membrane A has a cross-linked structure and quaternary pyridinium group, resulting from the reaction of CMS and 2M5VP.

Figure 3 shows the infrared spectra of base membrane A. Absorption band at  $1600\text{ cm}^{-1}$ , assigned to aromatic or pyridine group, is observed in the cases of poly-CMS and poly-2M5VP. However, a strong new absorption band is observed at  $1625\text{ cm}^{-1}$  in the base membrane A. The base membrane A contains NBR and the PVC cloth, but they have no absorption band at  $1625\text{ cm}^{-1}$ .<sup>16</sup> Then the strong absorption band at  $1625\text{ cm}^{-1}$  is assigned to the quaternary pyridinium group which shifts from  $1600\text{ cm}^{-1}$ .<sup>17</sup> This proves that the base membrane A contains the quaternary pyridinium group and the cross-linking structure.

Figure 4 shows the relation of the monomer composition in the recipe to  $P_{2\text{M5VP}}$ ,  $P_{\text{CMS}}$ , and  $D_{\text{cross}}$ . It is expected that the 2M5VP content dominates  $D_{\text{cross}}$  when the 2M5VP content is smaller than 50% and, on the other hand, the CMS content dominates  $D_{\text{cross}}$  when the 2M5VP content is larger than

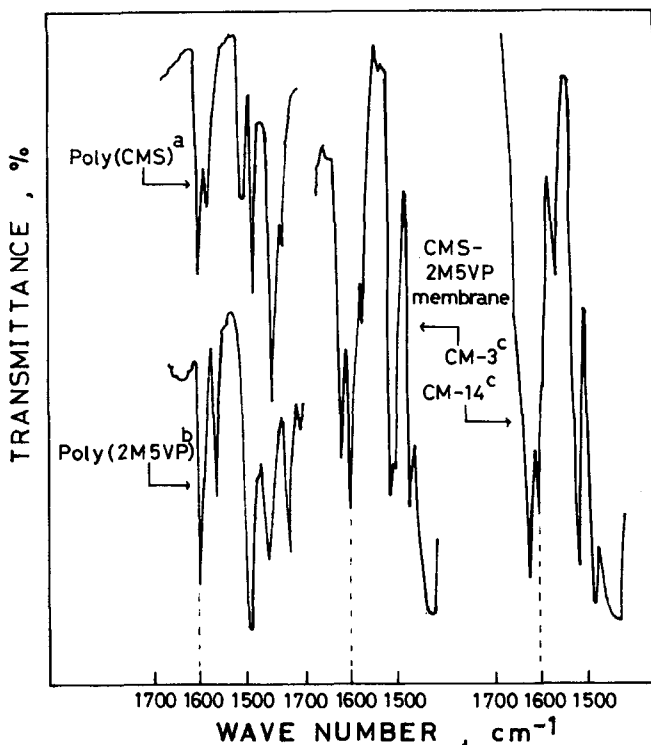


Fig. 3. IR spectra of the CMS-2M5VP membranes. (a) Prepared by bulk polymerization at  $60^\circ\text{C}$  by using BPO. (b) Prepared by bulk polymerization at  $60^\circ\text{C}$  by using AIBN. (c) Including NBR rubber (3 wt%) and polyvinylchloride (backing fabric).

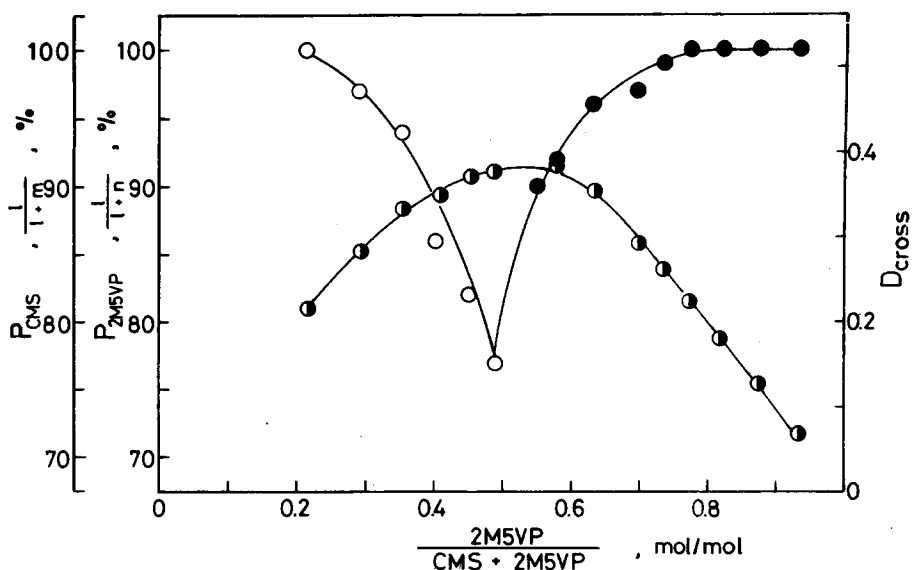


Fig. 4. Relation between the 2M5VP content of the monomer mixture and participation ratio of 2M5VP ( $P_{2M5VP}$ , ○) and of CMS ( $P_{CMS}$ , ●) with cross-linking or cross-linking degree ( $D_{cross}$ ) in the membranes (●).

50%. Also, if the monomers react completely to each other to form the cross-linking unit, the membrane should have the fairly large cross-linking degree.

Evidently, when the amounts of CMS and 2M5VP are approximately equimolar,  $D_{cross}$  becomes maximum. The participation ratio of the lesser component with the cross-linking increases to 100% with the decrease in the amount of the lesser component, and the proportion of the monomers participating with the cross-linking reaction decreases when approaching to the equimolar amount of CMS and 2M5VP. Presumably, the following reactions occur competitively and at random.

1. Quaternization of 2M5VP with CMS.
2. Radical copolymerization of CMS, 2M5VP, and the divinyl compound formed by the quaternization of 2M5VP with CMS.
3. Quaternization of the copolymerized CMS unit with the copolymerized 2M5VP unit.
4. Reaction of the copolymerized CMS and 2M5VP units with CMS and 2M5VP, respectively.
5. Anion polymerization of the Kabanov type.

The copolymerization mechanism is too complex to be elucidated clearly.

Although the reaction 1 should be rapid and the polymerization should proceed by the reactions 2 and 5, their partition ratios are obscure now. Here, we could not observe rapid polymerization of 2M5VP and CMS by their mixing and we could succeed in coating the monomer mixture onto the PVC cloth. This means that reaction 5 is relatively slow and reaction 2 should be dominant.

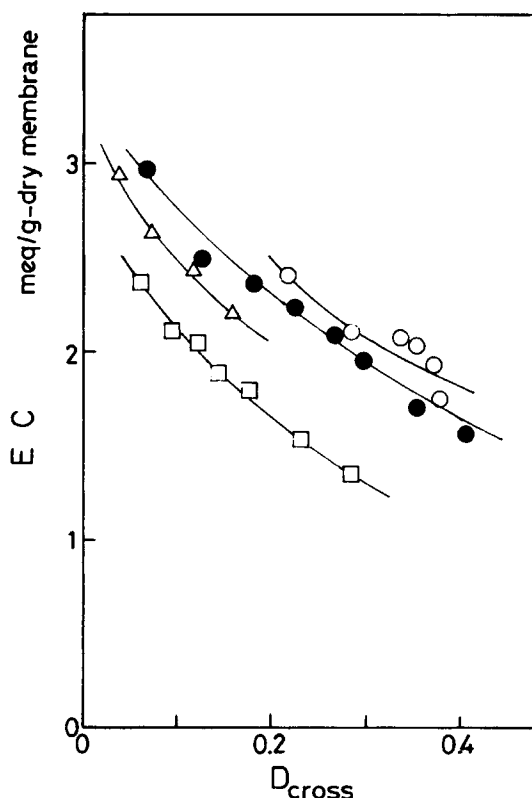


Fig. 5. Relation between  $D_{cross}$  and ion exchange capacity (EC): (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (△) 2M5VP-DVB membranes.

Also, reactions 3 and 4 should be less participating than reactions 1 and 2, regarding the formation of the cross-linking unit. Furthermore, the development of the three-dimensional structure should make reactions 3 and 4 uneasy.

However, it is noteworthy that the CMS-2M5VP membrane is more tightly cross-linked in comparison with the CMS-DVB and 2M5VP-DVB membranes, as will be described later.

Figures 5–9 show the relation between  $D_{cross}$  and the membrane properties. In the cases of the membranes prepared using DVB, the increase in the DVB content increases R and FC, and decreases EC, WC, and  $D_{NaCl}$ . The CMS-2M5VP membrane also shows a similar tendency to the CMS-DVB and 2M5VP-DVB membranes.

In the relation to  $D_{cross}$ , the value of EC is as follows: The CMS-2M5VP membrane ( $m > n$ ) > the CMS-2M5VP membrane ( $m < n$ ) > the 2M5VP-DVB membrane > the CMS-DVB membrane and also the value of WC is reasonably similar. These results are owing to the structure of the CMS-2M5VP membrane of which the cross-linking unit itself contains the anion exchange group.



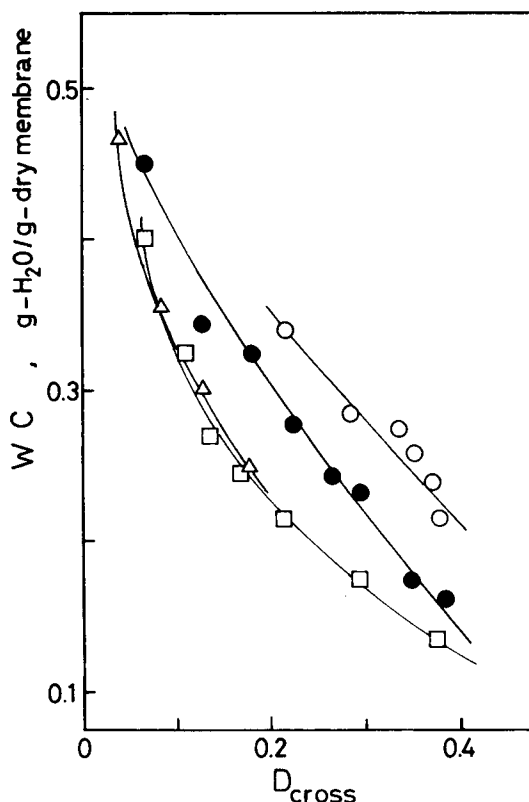


Fig. 6. Relation between  $D_{\text{cross}}$  and water content (WC): (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (△) 2M5VP-DVB membranes.

It is noteworthy that the tendencies of the CMS-2M5VP membrane ( $m > n$ ) are outstandingly preferable. For example,  $R$  is smaller than those of the others relating to  $D_{\text{cross}}$  and  $FC$  is smaller. This is explained as follows: the residual 2M5VP unit in the membrane, not participating with the cross-linking, contributes to the membrane properties as a weakly basic anion exchange group because the membranes were treated with 1.0  $N$  HCl solution. The effect of the copolymerizabilities of CMS or 2M5VP with the divinyl compound, resulting from the reaction of CMS and 2M5VP, are obscure now.

Conversely, in the case of the CMS-2M5VP membrane treated with  $\text{CH}_3\text{I}$  ( $n > m$ ), the CMS unit has no anion exchange capacity. Therefore, it can be anticipated that the successive treatment of the base membrane A with  $\text{CH}_3\text{I}$  and  $(\text{CH}_3)_3\text{N}$  could result in more excellent anion exchange membrane. Furthermore, transport number is one of the most important properties and is related to  $FC$ . The transport number of  $\text{Cl}^-$  in all the membranes is  $> 0.98$ , estimated at  $25^\circ\text{C}$  by electro dialysis in a 0.5  $N$  NaCl aqueous solution with current density, 20  $\text{mA}/\text{cm}^2$ . Thus, the CMS-2M5VP membrane is proved to have good properties, because of the presence of the anion exchange group in the cross-linking unit itself.

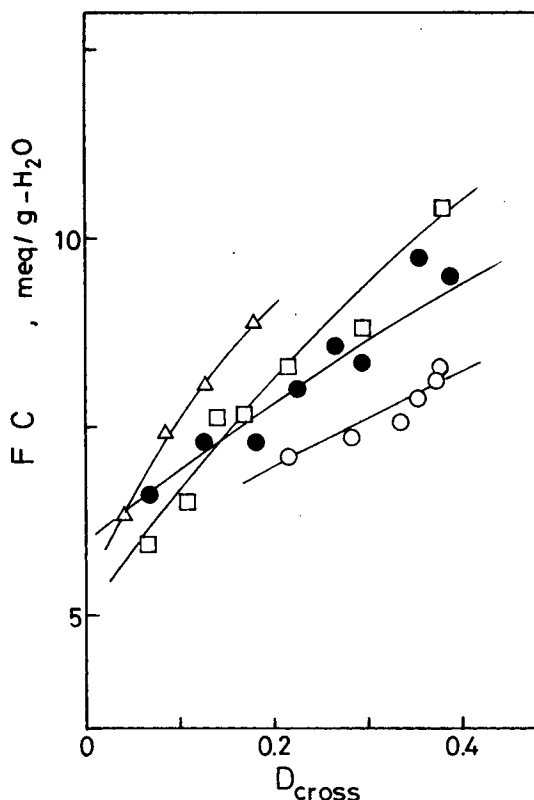


Fig. 7. Relation between  $D_{\text{cross}}$  and fixed ion concentration (FC): (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (Δ) 2M5VP-DVB membranes.

Figure 10 shows the relation between  $D_{\text{NaCl}}$  and FC of the membranes. The tendencies of the CMS-DVB and 2M5VP-DVB membranes are shown as the same line.  $D_{\text{NaCl}}$  of the CMS-2M5VP membranes becomes smaller than those of the others with increasing FC. This result is meaningful for practical applications, because permeability could be improved by these membranes. The difference in the tendencies of the CMS-DVB and 2M5VP-DVB membranes from the CMS-2M5VP membranes might be ascribed to the differences in their cross-linking structure and the distribution of the cross-linking, but details are still obscure.

Figure 11 shows an electron microphotograph of the base membrane for the CMS-DVB membrane, the poly(CMS-DVB) portion is white and the NBR-containing portion is stained. Evidently, the bright domain size is distributed over a rather large range and becomes smaller with an increase in the DVB content. The stained area is probably too large to be explained by the low NBR content of the membranes. The suggested reason is as follows: the electron microphotograph shows only the membrane portion without PVC cloth. NBR could not penetrate into the PVC cloth but the monomers could. Therefore the membrane portion without PVC cloth should include more NBR than the PVC cloth portion.

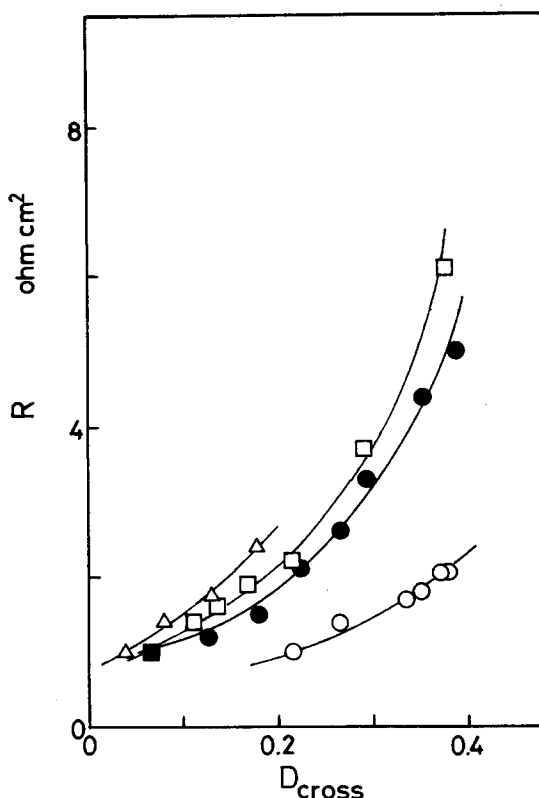


Fig. 8. Relation between  $D_{cross}$  and electric resistance ( $R$ ): (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (△) 2M5VP-DVB membranes.

Figure 12 shows the electron microphotographs of the 2M5VP-DVB membranes.

Although the contrast is rather obscure because the poly(2M5VP-DVB) phase could be stained with osmium tetroxide, the spherical poly(2M5VP-DVB) portion is finer than those of the CMS-DVB membranes. The poly(2M5VP-DVB) domain also becomes relatively smaller with the increase in the DVB content. The difference in the patterns between the two systems might be ascribed to the difference in affinity of 2M5VP and CMS with NBR. These results show the heterogeneity of the CMS-DVB and 2M5VP-DVB membranes. DVB is more preferentially incorporated in the three-dimensional network at the earlier stage of copolymerization and, consequently, phase separation should occur rapidly, hence the domain becomes smaller. Loosely cross-linked copolymers are formed at the later stage of copolymerization and, consequently, phase separation might be delayed with the decrease in the DVB concentration, so the resultant domain becomes larger.

Figure 13 shows the electron microphotographs of the 2M5VP-CMS membranes.

Although the composition of the domain was not identified because of the complex copolymerization mechanism, the domain size shows a tendency

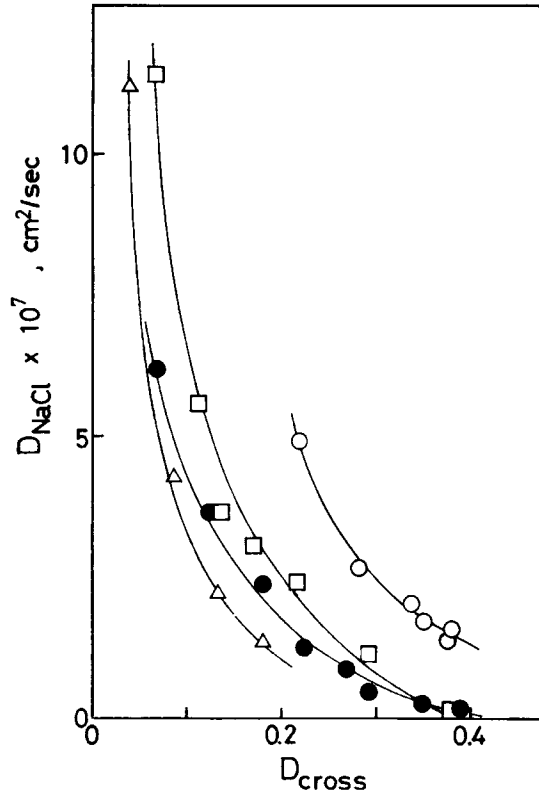


Fig. 9. Relation between  $D_{cross}$  and apparent diffusion coefficient ( $D_{NaCl}$ ): (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (Δ) 2M5VP-DVB membranes.

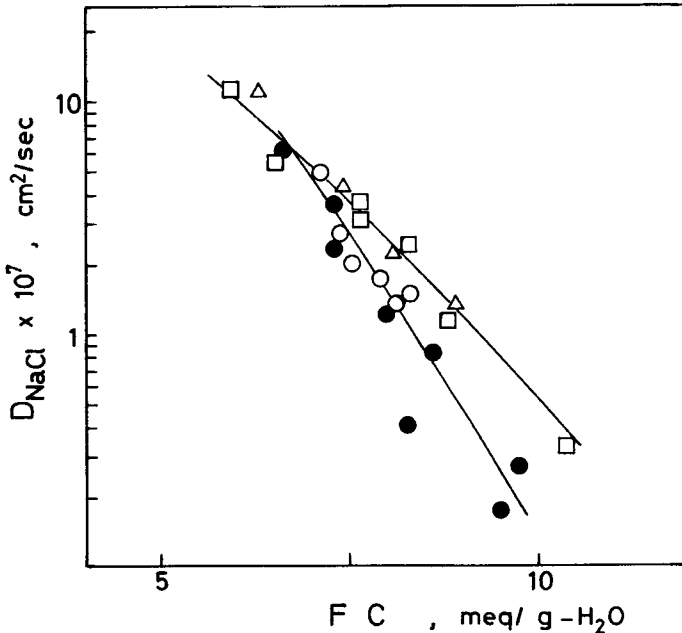


Fig. 10.  $D_{NaCl}$  vs.  $FC$ : (○) CMS-2M5VP membranes ( $m > n$ ); (●) CMS-2M5VP membranes ( $m < n$ ); (□) CMS-DVB membranes; (Δ) 2M5VP-DVB membranes.

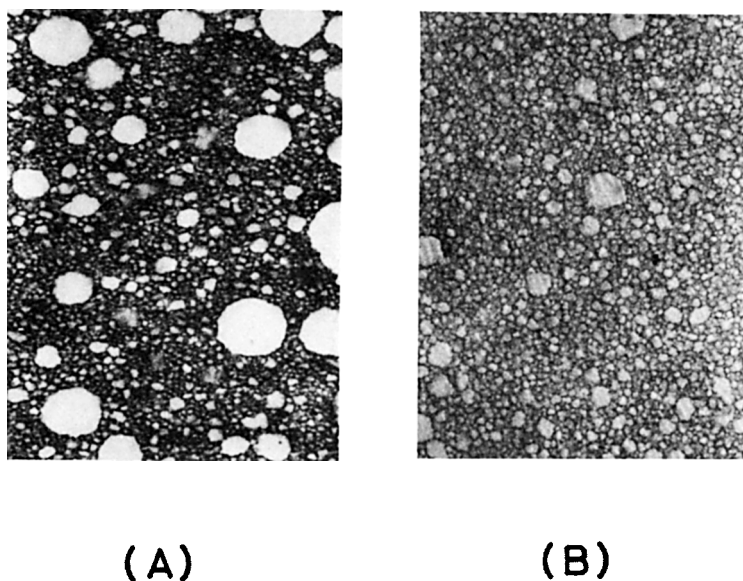


Fig. 11. Electron microphotograph of the base membrane B for the CMS-DVB membranes: (A), CD-1; (B), CD-7.

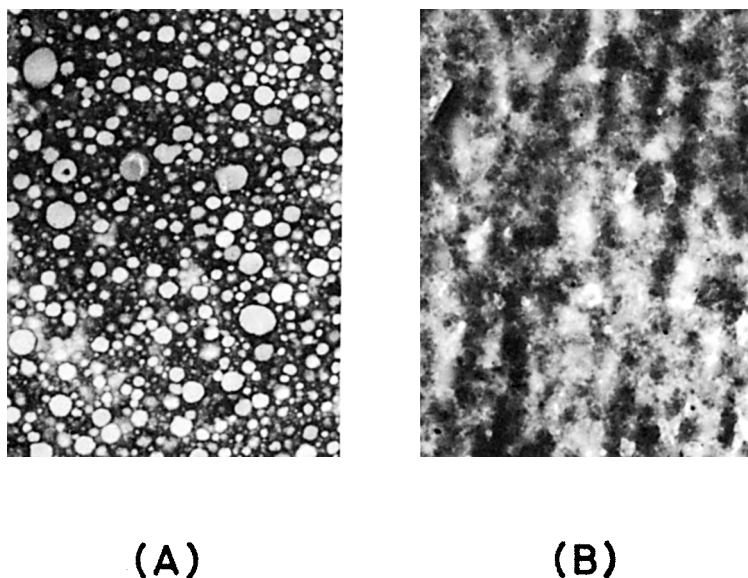
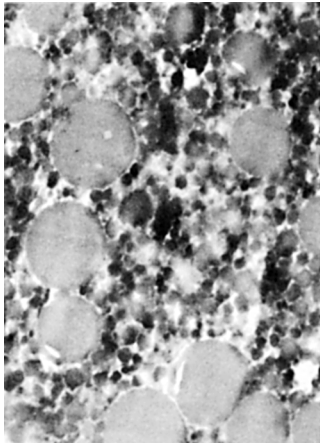


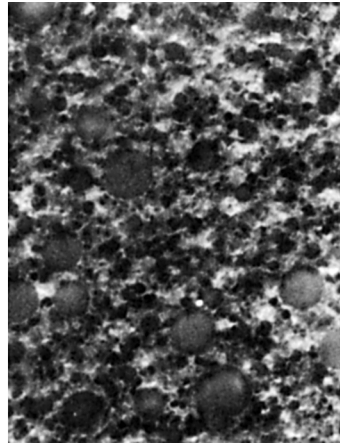
Fig. 12. Electron microphotograph of the base membrane C for the 2M5VP-DVB membranes: (A), MD-1; (B), MD-4.

similar to those of the CMS-DVB and 2M5VP-DVB membranes in relation to the quantity of the divinyl compound resulting from the reaction of CMS and 2M5VP.

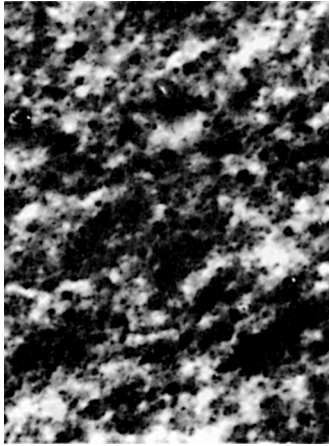
As previously described, several reactions should occur in copolymerization of CMS with 2M5VP. Presumably, quaternization is relatively fast but anion



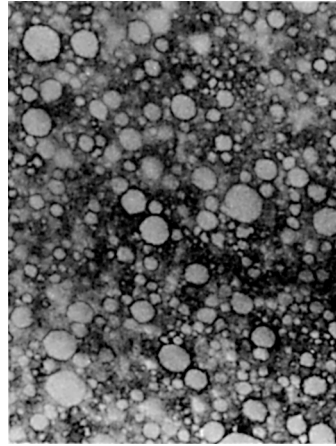
(A)



(B)



(C)



(D)

Fig. 13. Electron microphotograph of the base membrane A for the CMS-2M5VP membranes: (A), CM-1; (B), CM-6; (C), CM-8; (D), CM-14.

polymerization of the Kavanov type is relatively slow. Thus, the dominant reaction is the radical copolymerization of CMS, 2M5VP, and the divinyl compound. Therefore, the photographs of these membranes can be understood as follows.

Assuming that the quantity of the divinyl compound participating in the radical copolymerization increases with approaching the equimolar amount of CMS and 2M5VP, polymerization of the divinyl compounds occurs predominantly, so the size of the domain becomes smaller and more uniform owing to the rapid phase separation. On the other hand, the radical copolymerization of the divinyl compounds with CMS or 2M5VP predominantly occurs with a

decrease in the amount of the divinyl compound, so the size of the domain distributes appreciably.

Now, the details of the copolymerization of the divinyl compounds with CMS or 2M5VP are unknown. However, it is elucidated that the CMS-2M5VP membranes also have heterogeneity in the cross-linking structure.

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