

Modification of Cation Exchange Membrane by Grafted Poly(4-vinyl-*N*-methylpyridinium-iodide)

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Synopsis

It is well known that cation exchange membranes, having a very thin layer of a cationic polyelectrolyte on the membrane surface, have preferential permselectivity for monovalent cations in a monovalent-divalent cations system. We studied the relationship between preferential permselectivity and molecular structure of the cationic polyelectrolyte. Grafted poly(4-vinyl-*N*-methylpyridinium-iodide) was used and was compared with poly(4-vinyl-*N*-methylpyridinium-iodide). The backbone polymers were poly(styrene-co-*p*-benzylstyrene) and poly(benzyl), onto which 4-vinylpyridine was grafted by anionic polymerization and then quaternized with CH₃I. The grafted poly(4-vinyl-*N*-methylpyridinium-iodide) is effective in making the cation exchange membrane preferentially permselective for Na⁺ in a Na⁺ - Ca²⁺ system and is more preferable than poly(4-vinyl-*N*-methylpyridinium-iodide) in terms of electric resistance of the membrane. However, the relationship between the molecular structure of the cationic polyelectrolyte and the durability of the preferential permselectivity is not clear.

INTRODUCTION

In electro dialytic concentration of sea water by ion exchange membranes, preferential concentration of monovalent cations (Na⁺, K⁺, and Cl⁻) is beneficial. It is well known that the formation of a very thin layer of a cationic polyelectrolyte results in preferential permselectivity for monovalent cations.¹ Some cationic group should be converted to polysalt by reaction with sulfonic groups on the membrane surface and other cationic groups should be effective as a barrier for permeation of divalent cations (Ca²⁺ and Mg²⁺). This is due to the difference in the electrostatic repulsion between the cationic barrier-monovalent cations system and the cationic barrier-divalent cations system.² Many cationic polyelectrolytes have been studied as modifiers for cation exchange membranes.³ However, little has been reported on the relationship between the molecular structure of the cationic polyelectrolyte and preferential permselectivity. Therefore, we have prepared graft polymers of 4-vinylpyridine (4-VP): 4-vinylpyridine was grafted onto poly(styrene-co-*p*-benzylstyrene) [poly(st-co-*p*-BSt)] and poly(benzyl) by anionic polymerization and then quaternized with CH₃I. The effectiveness of these graft polymers as membrane modifiers was investigated in comparison with that of poly(4-vinyl-*N*-methylpyridinium-iodide).

EXPERIMENTAL

Synthesis of *p*-Benzylstyrene

p-Benzylstyrene (*p*-BSt) was prepared according to the method by Marvel et al⁴ as follows:

Into a suspension of anhydrous aluminum chloride (1.5 mole) in carbon disulfide (860 mL), acetyl chloride (1.5 mole) was added in 15 min with vigorous stirring and cooling in an ice bath. Diphenylmethane (1.5 mole) was added dropwise over 1 h. The resultant mixture was stirred for 6 h and then poured into the mixture of ice and an aqueous solution of hydrochloric acid with stirring. The carbon disulfide solution was separated and washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. The solution obtained was dried over anhydrous sodium sulfate, filtered, and the carbon disulfide was distilled off. Thus *p*-benzylacetophenone (1.26 mole) was obtained (yield 84%). To a suspension of lithium aluminum hydride (1.32 mole) in 2,000 mL of diethyl ether, which had been treated in advance by sodium wire, *p*-benzylacetophenone (1.26 mole) was added over 3 h with vigorous stirring and cooling in an ice bath. The product was stirred at 35°C for 5 h and methanol was added to decompose the excess lithium aluminum hydride. The product was poured into a mixture of ice and dilute hydrochloric acid with stirring. The ether solution was separated and washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. The solution was then dried over anhydrous sodium sulfate filtered and the ether was distilled off. Thus 1-(*p*-benzylphenyl)ethanol (0.47 mole) in dimethyl sulfoxide (380 mL) was dehydrated by trichloroacetic acid (0.12 mole) and zinc chloride (0.14 mole) at 170°C for 30 min and was poured into ice and water. The product was extracted with diethylether and the extracted solution was dried over anhydrous sodium sulfate filtered, and the ether was distilled off. Thus, *p*-benzylstyrene (*p*-BSt) (0.28 mole) was obtained (yield 67%). *p*-BSt was characterized by ¹H nuclear magnetic resonance (NMR) and infrared (IR). Characteristic peaks are as follows.

¹H-NMR (60 MHz): δ = 3.9 (s, 2H, phCCH_2ph), 5.2 (dd, $J=1.6$, 10.5 Hz, H, phCCH_2 *trans*), 5.6 (dd, $J = 1.6$, 18 Hz, H, ph-CCH_2 *cis*), 6.7 (dd, $J = 10.5$, 18 Hz, H, phCCHC), 7.0–7.2 (m, 4H, CArHC), 7.2–7.4 (m, 5H, CArH);

IR: 3000, 1630, 1600, 1500, 1400, 1100, 990, 900, 800, 740, and 700 cm^{-1} . These results agree with the theoretical values.

Synthesis of Poly(St-co-*p*-BSt)

Copolymerization of *p*-BSt and St was carried out by using $\alpha\alpha'$ -azobisisobutyronitrile (AIBN) in toluene for 18 h at 70°C under nitrogen atmosphere: The *p*-BSt/St molar ratios were 12.5/87.5 (A-1), 50/50 (A-2), 75/25 (A-3), and 100/0 (A-4). The toluene solutions of these polymers were poured into a large excess of methanol and the precipitated polymers were filtered and dried under vacuum. These polymers were light yellow powders. To obtain the copolymer with different molecular weight, the resultant polymers were fractionated. Methanol was added dropwise to the benzene solution of the copolymer until the solution became turbid and then an apparent phase separation appeared. After the phase separation was recognized, the lower

phase was separated and the copolymer was recovered. This procedure was repeated and poly(St-co-*p*-BSt) having different molecular weights was obtained.

Synthesis of Poly(benzyl)

Into a mixed solution of anhydrous aluminum chloride (0.38 mole) and diphenylmethane (0.5 mole), benzylchloride (1 mole) was added over 75 min with vigorous stirring and cooling in ice bath. The resultant solution was stirred for 30 min and poured into ice and water with stirring. The product was extracted by benzene and washed successively with dilute hydrochloric acid, aqueous sodium carbonate and water. After the benzene solution was dried over anhydrous sodium sulfate, benzene, diphenylmethane (b.p. 262°C), and dibenzylbenzene (b.p. 350-380°C) as byproducts were distilled under vacuum. The poly(benzyl) was dissolved in benzene and the resultant solution was poured into methanol to precipitate the poly(benzyl). The purified poly(benzyl) was recovered and dried under vacuum.

Graft Polymerization

The methylene groups of the backbone polymers are reactive and the C—H bond can be easily transformed to C—Li bond by treating with *n*-butyllithium (*n*-BuLi).⁵ Then 4-VP was grafted at the C—Li bond by anionic polymerization. Tetrahydrofurane (THF), which had been dehydrated by sodium wire and then distilled in the presence of lithium aluminum hydride, was used as the solvent. The lithiumation of diphenyl methylene groups proceeds quantitatively if *n*-BuLi is used in large excess. The excess *n*-BuLi reacts with THF and is inactivated if it is allowed to stand for more than 15 h at room temperature.⁵ Therefore, the isolation and purification of the lithiumated polymer was not necessary. The lithiumation of the polymer and the graft polymerization was done under vacuum at $-70 \sim -78^\circ\text{C}$ using a methanol-dry ice bath. Excess *n*-BuLi was inactivated by THF under dry nitrogen atmosphere at room temperature. The reaction product was poured into water, and the resultant polymer was recovered and washed with methanol and dried under vacuum. Light brown powder was obtained.

Synthesis of Poly(4-VP)

Poly(4-VP) was obtained by radical polymerization of 4-VP in ethanol and fractionated by methanol-acetone system. Thus poly(4-VP) having different molecular weight were obtained.

Characterization of Graft and Linear Polymers

The molecular weight of the polymers was determined by intrinsic viscosity and gel permeation chromatography (GPC). The molecular weight distribution was measured by GPC. The measurement of the viscosity was carried out by using an Ubbelohde-type viscometer at 25°C in ethanol solution. From the value of the intrinsic viscosity, the mean molecular weight of the polymers

was calculated by the following equation.⁶

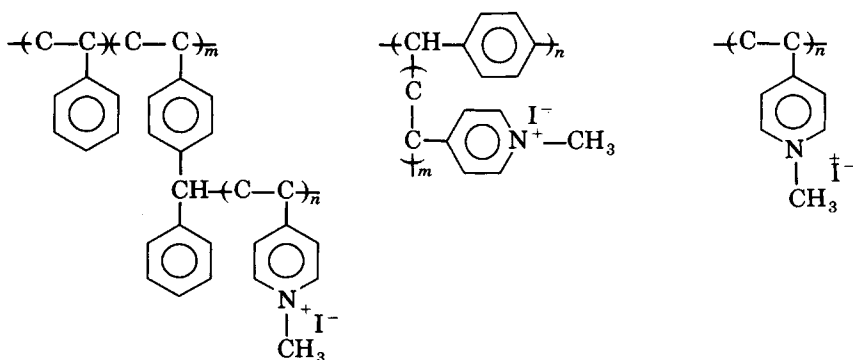
$$[\eta] = 2.5 \times 10^{-4} \bar{M}^{0.68}$$

where $[\eta]$ is the intrinsic viscosity. \bar{M} is the mean molecular weight. GPC measurement was carried out with the aid of Hitachi 633 type high-speed liquid chromatography, Hitachi 638-41 type variable wave length ultraviolet (UV) monitor and 833 type data processor. The measurement condition for the backbone polymer was follows: column, SHOWDEX A-804; eluent, trichloromethane; flow rate of eluent, 1.0 mL/min; wave length of the detector, UV 254 nm. Also the measurement condition for the graft polymer and poly(4-VP) was as follows: column, TOYOSODA G-400 PW; eluent, 1/15 N H_3PO_4 - 1/10 N KCl mixed aqueous solution; flow rate of eluent, 1.0 mL/min; wave length of the detector, UV 265 nm.

Quaternization of the Graft and Linear Polymer

The graft and linear polymer were quaternized with methyl iodide in a methanol-nitroethane mixed solvent (1 : 1 in volume) for 70 h at room temperature. The degree of quaternization was determined by IR spectrum, using the adsorptions at 980 cm^{-1} assigned to pyridine ring and at 1640 cm^{-1} assigned to quaternized pyridine ring. In this study, almost all 4-VP units were quaternized.

Thus, the polymers as modifiers for cation exchange membranes were prepared and their structure are shown as follows.



Poly(St-co-*p*-Bst)-graft-Poly(4-vinyl-*N*-methylpyridinium-iodide)

P-A

Poly(benzyl)-graft-Poly(4-vinyl-*N*-methylpyridinium-iodide)

P-B

Poly(4-vinyl-*N*-methylpyridinium-iodide)

P-C

Procedure for Membrane Modification

Cation exchange membrane. The cation exchange membrane used is NEOSEPTA CM-1 (Tokuyama Soda Co., Ltd), which was treated with aqueous HCl and NaCl solutions before use.

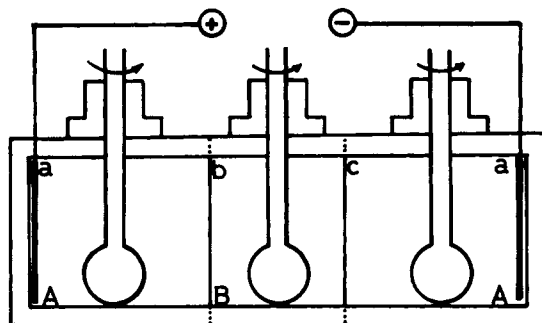


Fig. 1. Cell for the modification of the membrane (a) Ag-AgCl electrode (b) anion exchange membrane ($2 \times 5 \text{ cm}^2$) (c) cation exchange membrane to be modified ($2 \times 5 \text{ cm}^2$).

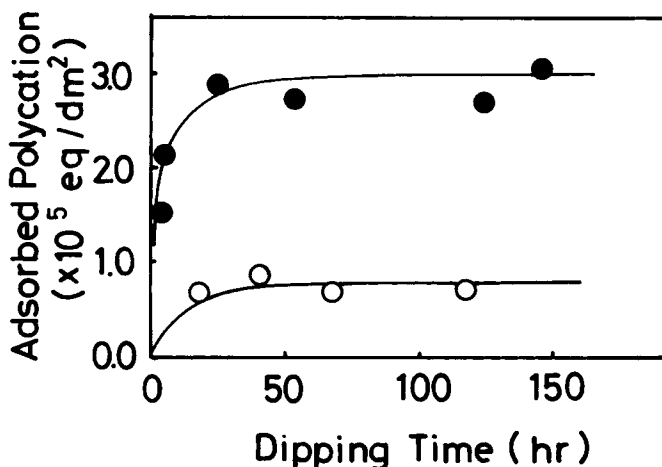


Fig. 2. Relationship between the dipping time and the quantity of adsorbed polycations (poly-4-vinyl-*N*-methylpyridinium-iodide). The cation exchange membrane ($7 \times 10 \text{ cm}^2$) was dipped in 200 ppm aqueous solution at 30°C (●) M_w 2600 (○) M_w 16,000.

Current-passing method. Figure 1 shows the cell used for the modification of the membrane by the current-passing method. The B compartment (100 mL) was filled with a 5000 ppm aqueous solution of the quaternized polymer and the A compartment ($130 \text{ mL} \times 2$) were filled with a 0.5 N NaCl aqueous solution. Then the current was passed through the membrane with 0.3 A/dm^2 for 25 min. The membrane was washed with water before using.

Dipping method. We preliminarily confirmed that the dipping time of 20 h at 30°C is enough to attain equilibrium of the adsorbed amount of the poly(4-vinyl-*N*-methylpyridinium-iodide), as shown in Figure 2. Therefore, the membrane ($7 \times 7 \text{ cm}^2$) was dipped in a 5,000 ppm aqueous solution (500 mL) of the quaternized polymer for 24 h at 45°C with stirring (100 rpm). The modified membrane was washed with water before use.

Measurement of $P_{\text{Na}}^{\text{Ca}}$

Figure 3 shows the cell used for the measurement of $P_{\text{Na}}^{\text{Ca}}$. Both compartments were filled with a 130 mL of the aqueous solution of 0.25 N NaCl and

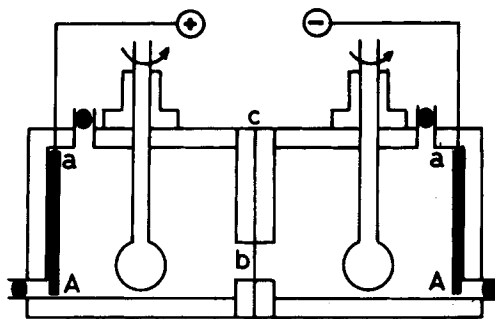


Fig. 3. Cell for the measurement of P_{Na}^{Ca} : (a) Ag-AgCl electrode (b) modification face of the membrane (c) modified membrane ($2 \times 5 \text{ cm}^2$).

0.25 N CaCl_2 . After the electro dialysis under the current density (2 A/dm^2) at 30°C for 1 h, the preferential permselectivity was defined by the following equation.²

$$P_{Na}^{Ca} = \frac{T_{Ca}/T_{Na}}{C_{Ca}/C_{Na}}$$

where C_{Na} = the concentration of Na^+ in the solution before electro dialysis, C_{Ca} = the concentration of Ca^{2+} in the solution before electro dialysis, T_{Na} = transport number of Na^+ , T_{Ca} = transport number of Ca^{2+} .

Measurement of the Durability of Permselectivity

The modified membrane was dipped in a 0.5 N NaCl aqueous solution for 80–90 h at room temperature with stirring. After the membrane was washed with water, P_{Na}^{Ca} was measured and compared with the P_{Na}^{Ca} before the treatment. The durability factor (D) was calculated as follows.

$$D = \frac{P_{Na}^{Ca} \text{ after the durability test}}{P_{Na}^{Ca} \text{ before the durability test}}$$

Electric Resistance of the Modified Membrane

After the modified membrane was dipped in a 0.5 N NaCl aqueous solution for 4 h, the electric resistance of the membrane was measured at 25°C in a 0.5 N NaCl aqueous solution under alternating current (1 KHz/s).

RESULT AND DISCUSSION

Preparation of the Backbone Polymers

Since *p*-benzylstyrene (*p*-BSt) is a derivative of styrene (St), the copolymerizability of *p*-BSt and St is presumed to be good. So, it is reasonably presumed that *p*-BSt is incorporated into the copolymer with the same ratio as that of the recipe.

TABLE I
 Molecular Weight of Fractionated Poly(St-co-*p*-BSt)

Name	No	<i>p</i> -BSt/St ^a	\bar{M}_w^b	Name	No	<i>p</i> -BSt/St	\bar{M}_w
A-1	1		100000	A-3	7		15500
	2		48000		8		10000
	3	12.5/87.5	40000		9		9000
	4		18000		1		73000
	5		14500		2		68000
A-2	6		5000	3	75.0/25.0	40000	
	1		78000	4		19000	
	2		66000	5		14000	
	3	50.0/50.0	53000	6		9000	
	4		40000	A-4	1	100.0/0	2800
	a5		34000		2		1940
	6		2200				

^aRatio of the monomer in the recipe.

^bWeight average molecular weight determined by GPC.

The result of the fractionation of poly(St-co-*p*-BSt) is shown in Table I. Figure 4 shows that the molecular weight distribution of the fractionated polymers are very narrow. Also, Figure 5 shows the relationship between the *p*-BSt unit content in the recipe and the ratio of the peak height ($800\text{ cm}^{-1}/750\text{ cm}^{-1}$) of the IR spectrum of the fractionated polymer (A-1-3, A-2-4, A-3-3, A-4-1). The peak at 800 cm^{-1} is assigned to disubstituted benzene and the peak at 750 cm^{-1} is assigned to monosubstituted benzene. The ratio of the peak height ($800\text{ cm}^{-1}/750\text{ cm}^{-1}$) of the fractionated polymers linearly increases with the increase of the *p*-BSt content in the recipe. This result indicates that the *p*-BSt is incorporated into the copolymer

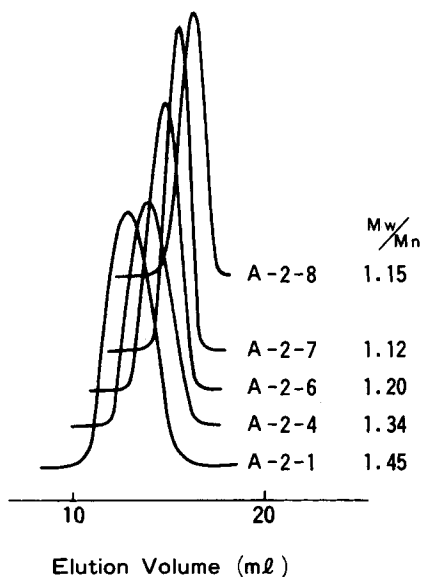


Fig. 4. Molecular weight distribution of fractionated poly(St-co-*p*-BSt).

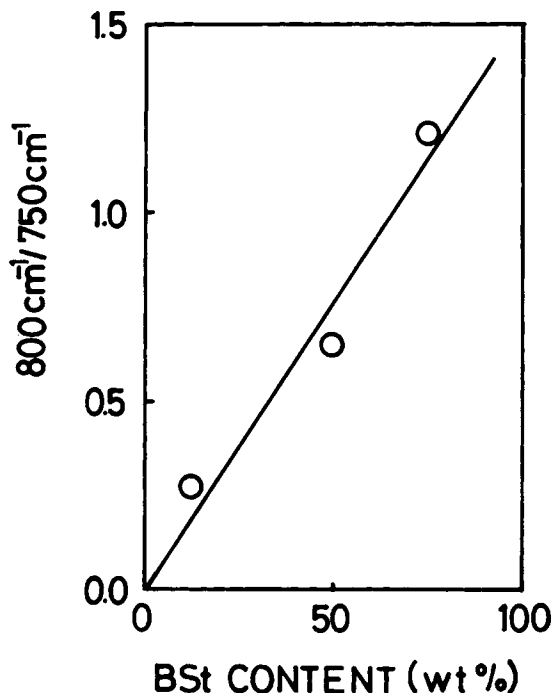


Fig. 5. Relationship between the *p*-BSt unit content in the recipe for the copolymerization of St and *p*-BSt and the ratio of the peak height ($800/750 \text{ cm}^{-1}$) of IR spectrum of the fractionated polymers of the poly(St-co-*p*-BSt): (A-1-3), (A-2-4), (A-3-3), (A-4-1) were used.

as presumed. Figure 6 shows that the molecular weight distribution of poly(benzyl) is not so narrow in comparison with those of poly(St-co-*p*-BSt) shown in Figure 4 and the mean molecular weight is about 600.

Preparation and Characterization of Graft Polymers

The THF solution of *n*-BuLi is light yellow, and the color changes to red by adding the backbone polymer. As soon as 4-VP is added dropwise, the polymerization rapidly proceeds and the product becomes insoluble in THF. This means that the anionic active center in the backbone polymer initiates

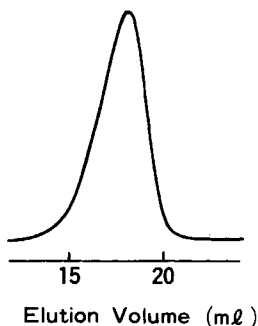


Fig. 6. Molecular weight distribution of poly(benzyl).

TABLE II
 Preparative Condition for Poly(St-co-p-BSt)-g-Poly(4VP) and Characterization

Sample name	Preparation condition			\bar{M}_w				
	Backbone ^a polymer	BuLi ^b (ml)	4VP (g)	Backbone ^c (A)	Branch ^d	Total branch(B)	Total (A + B)	B/A
A-1-5-a	A-1-5	50	12.8	14500	4700	75500	90000	5.1
A-2-7-a	A-2-7	60	39.6	15500	4700	245500	261000	15.9
A-2-7-b	A-2-7	60	19.8	15500	2360	122500	138000	7.9
A-2-9-a	A-2-9	60	11.5	9000	1370	41000	50000	4.6
A-3-8-a	A-3-8	78	12.8	12500	1170	63800	76300	5.1
A-4-1-a	A-4-1	934	12.5	2800	970	14000	16800	5.0
A-4-2-a	A-4-2	93	15.0	1940	1160	11660	13600	6.0

^a2.5 g.

^b1.55 M *n*-hexane solution.

^cWeight average molecular weight determined by GPC.

^dCalculated value from the quantity of the feed monomer:

$$\bar{M}_w(4VP) \times \frac{a}{A \times b \times 1/\bar{M}_w(p-BSt)}$$

a = 4vp quantity(mol) in the feed; b = weight fraction of p-BSt in the backbone polymer.

the anionic polymerization, which rapidly proceeds. Tables II and III show the preparative conditions and the characterization of the graft polymers. As described above, the resultant graft polymer becomes soluble resistant in THF as the polymerization proceeds. Then, the poly(4VP) branches with various polymerization degree might be formed in the same molecule. In order to confirm the graft structure, the values of $[\eta]$ vs the elution volume of GPC of poly(benzy)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) are plotted in Figure 7. Two curves are clearly different. This should be ascribed to the difference in the conformation of the polymers in solution. Namely, the random coil of poly(benzyl)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) should be smaller than that of poly(4-vinyl-*N*-methylpyridinium-iodide) when

 TABLE III
 Preparation Condition for Poly(benzyl)-g-poly(4VP) and Characterization

Name	Preparation condition				\bar{M}_w^a	$[\eta]^b$	\bar{M}_v^c	Branches ^d
	Backbone polymer(g)	BuLi (mL)	THF (mL)	4VP (g)				Backbone
B-1	2	72	100	10	8600	0.15	12700	5
B-2	2	72	100	20	29000	0.25	25700	10
B-3	2	72	100	15	16500	0.22	21400	7.5
B-4	2	72	100	15	6000	0.04	1550	7.5
B-5	2	72	100	7.5	12500	0.14	10700	3.3

^aWeight average molecular weight determined by GPC.

^bIntrinsic viscosity.

^cViscosity average molecular weight determined by $[\eta]$.

^dCalculated value from the quantity of the feed monomer.

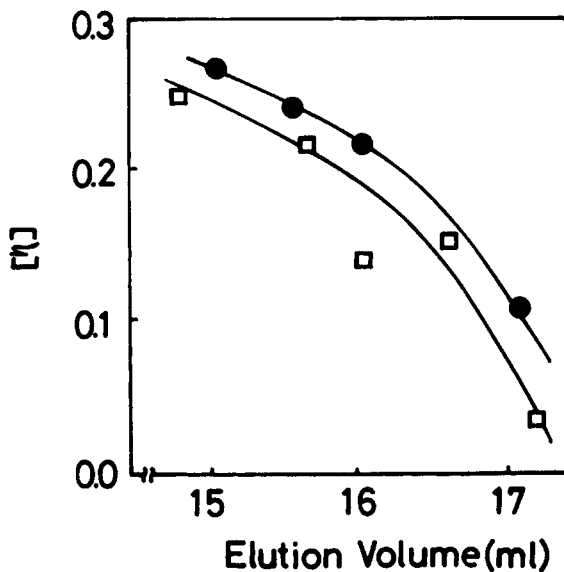


Fig. 7. Relationship between the elution volume of GPC and $[\eta]$ of pol(benzyl)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) (□) and poly(4-vinyl-*N*-methylpyridinium-iodide) (●).

the molecular weights are the same. Therefore, this should be ascribed to the structure of the graft polymer.

Preparation and Characterization of Poly(4VP)

Figure 8 shows the GPC chart of the linear poly(4VP) and Table IV shows the molecular weight. Linear poly(4VP), having different molecular weight

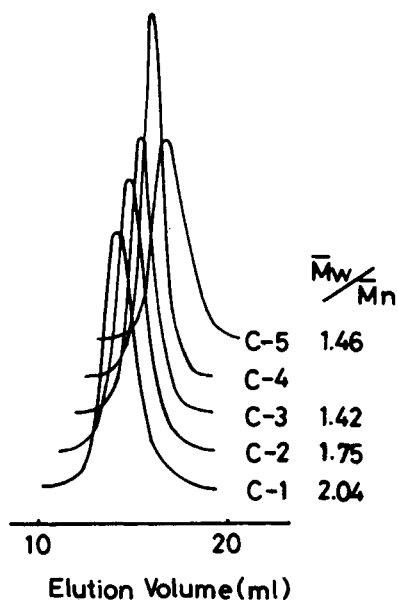


Fig. 8. Molecular weight distribution of the fractionated poly(4VP).

TABLE IV
 Molecular Weight of Poly(4VP)

Name	Mw ^a	Mn ^b	$[\eta]^c$	Mv ^d	Mw/Mn
C-1	46000	22500	—	—	2.04
C-2	24000	13700	0.27	28000	1.75
C-3	17000	12000	0.24	24000	1.42
C-4	12600	—	0.22	21500	
C-5	6400	4400	0.11	7500	1.46

^aWeight average molecular weight determined by GPC.

^bNumber average molecular weight determined by GPC.

^cIntrinsic viscosity.

^dViscosity average molecular weight determined by $[\eta]$.

and narrow molecular weight distribution, were prepared. These polymers were quaternized with CH_3I for the modifier.

MODIFICATION OF THE CATION EXCHANGE MEMBRANE

Figure 9 shows the relationship between the molecular weight of the poly(St-co-*p*-BSt)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) and the $P_{\text{Na}}^{\text{Ca}}$ values of the modified cation exchange membrane. In both the dipping method and the current-passing method, the $P_{\text{Na}}^{\text{Ca}}$ values decrease with decreasing molecular weight. Also, the current-passing method is evidently more effective than the dipping method. Figure 10 shows the relationship between the molecular weight of the three polymers (P-A, P-B, P-C), and the $P_{\text{Na}}^{\text{Ca}}$ values of the cation exchange membrane modified by the current-passing method. All the polymers show approximately similar tendencies and, also, the polymers with the molecular weight of $1-2 \times 10^4$ are most effective as modifiers. In the region of molecular weight larger than $1-2 \times 10^4$, the relation is similar to that shown in Figure 9. On the other hand, the $P_{\text{Na}}^{\text{Ca}}$ values increase with decreasing molecular weight in the region of molecular weight smaller than $1-2 \times 10^4$.

Figure 11 shows the comparison of the P-B polymers and the P-C polymers, regarding the relationship between the molecular weight of the polymers and the $P_{\text{Na}}^{\text{Ca}}$ values of the modified cation exchange membranes. No significant difference was observed between P-B and P-C polymers and, also, the current-passing method is clearly more effective.

Figure 12 shows the comparison of the P-B polymers and the P-C polymers, regarding the relationship between the molecular weight of the polymers and the durability factor (D) of the modified cation exchange membranes. Clearly, the current-passing method is more preferable in both cases of the P-B polymers and the P-C polymers. Also, the approximately similar tendencies are observed in both cases. It is very interesting that the D values of the membranes modified by the current-passing method are less than unity when the molecular weight is smaller than 3×10^4 . It means that the durability test makes the $P_{\text{Na}}^{\text{Ca}}$ value more preferable, but the detail is obscure.

Figure 13 shows the relationship between the molecular weight of the P-B and P-C polymers and electric resistances of the cation exchange membranes

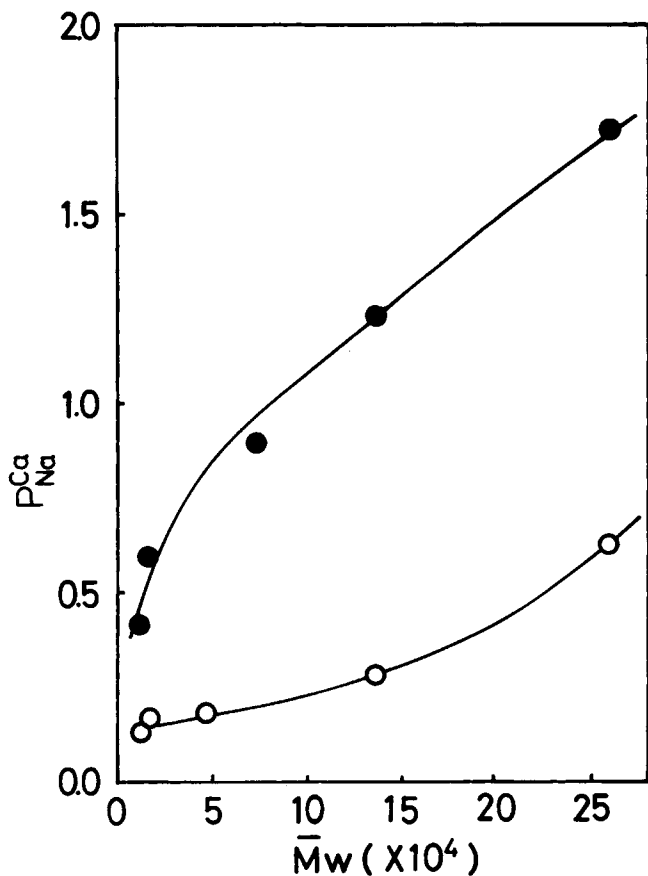


Fig. 9. Relationship between the molecular weight of poly(St-co-*p*-BSt)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) and P_{Na}^{Ca} ; (●-) dipping method, (○-) current-passing method.

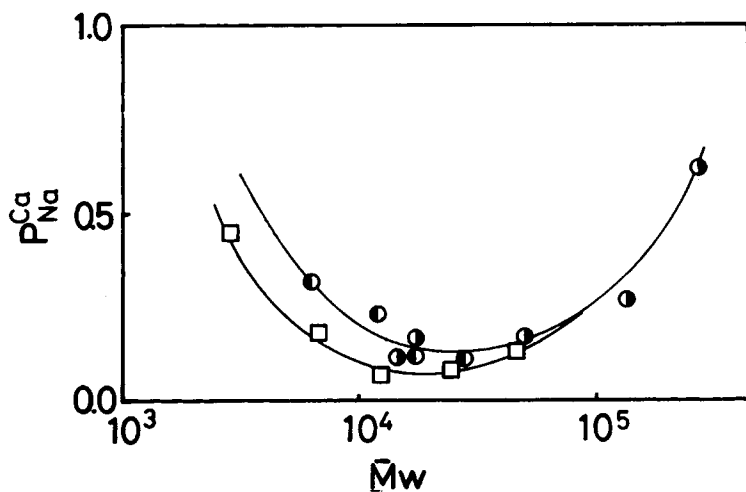


Fig. 10. Relationship between the molecular weight and P_{Na}^{Ca} in the case of the current-passing method: (□-) poly(4-vinyl-*N*-methylpyridinium-iodide), (○-) poly(St-co-*p*-BSt)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide), (●-) poly(benzyl)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide).

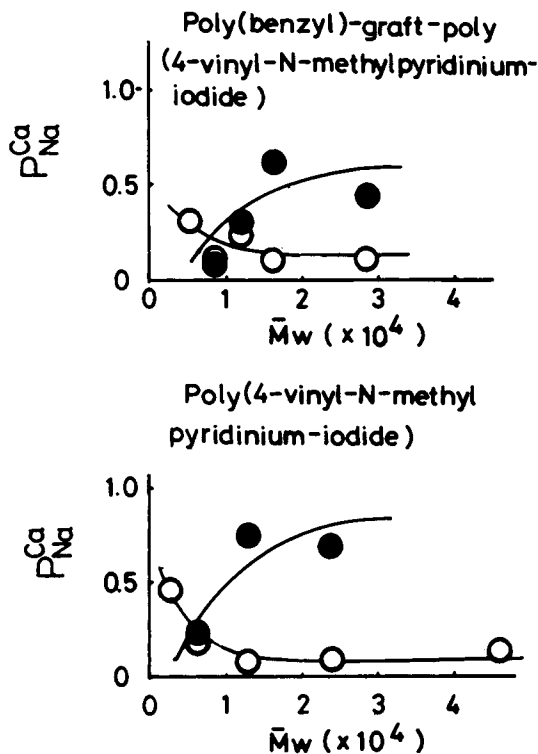


Fig. 11. Relationship between the molecular weight and P_{Na}^{Ca} of poly(benzyl)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) in comparison with poly(4-vinyl-*N*-methylpyridinium-iodide); (●) dipping method, (○) current-passing method.

modified by the current-passing method before and just after the durability test. Similar tendencies are observed, but the electric resistance in the case of the P-B polymers is a little larger than that in the case of the P-C polymers. When the molecular weight of the polymers is smaller than 6×10^3 , the electric resistance sharply increases with decreasing molecular weight, owing to soaking of the polymers into the membrane.

Figure 14 shows the relationship between the electric resistance of the cation exchange membrane, modified with the P-B and P-C polymers by the current-passing method, and the P_{Na}^{Ca} values. The P_{Na}^{Ca} values linearly decrease with decreasing electric resistance. Furthermore, when the electric resistance is the same, the modification with the grafted polymer (P-B polymers) endows the membranes with better P_{Na}^{Ca} values. The effectiveness of the cationic polymers as modifiers of cation exchange membranes can be explained as follows. The polymer in the bulk solution adheres to the membrane surface to form a very thin layer containing the cationic group, the quaternary pyridinium group. Some of the quaternary pyridinium groups combine with the sulfonic groups on the membrane surface and the others remain free. These free quaternary pyridinium groups are effective in forming the barrier which makes the permeation of the divalent cation more difficult. Also, some part of the polymer molecule would penetrate into the three-

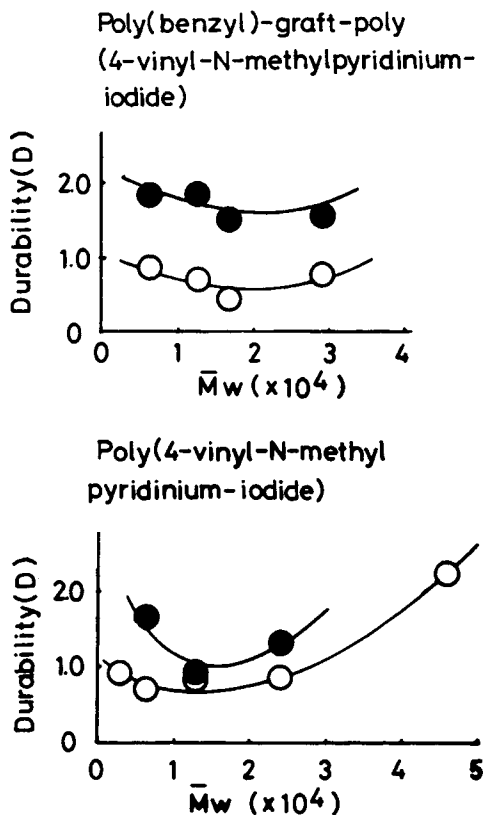


Fig. 12. Durability factor (D) of the modification by poly(benzyl)-graft-poly(4-vinyl-N-methylpyridinium-iodide) in comparison with poly(4-vinyl-N-methylpyridinium-iodide); (●) dipping method, (○) current-passing method.

dimensional matrix of the membrane surface and then the polymer molecule could be anchored.

The superior effectiveness of the current-passing method to the dipping method can be explained as follows. The polymer in the bulk solution is forced more rapidly to interact with the membrane surface because of the current-passing, and probably forms the thin layer with the tighter structure, which is more effective in modifying the membrane. The reason why there is the appropriate region of the molecular weight of the polymer is that the polymer with that molecular weight is just adequate to interact with the rigid membrane surface with less soaking into the membrane.

The superiority of the graft polymer to the linear polymer shown in Figure 14 could be ascribed to the conformation of the polymer molecule in relation to the ease of forming the tighter thin layer with more free quaternary pyridinium groups. However, we could not elucidate the details regarding the effectiveness of the graft polymers in terms of their structure.

We plan to study, in the near future, the relationships between the quantity of the polymer adhered onto the membrane surface, the quantities of the quaternary pyridinium groups which remain free or combine with the sulfonic

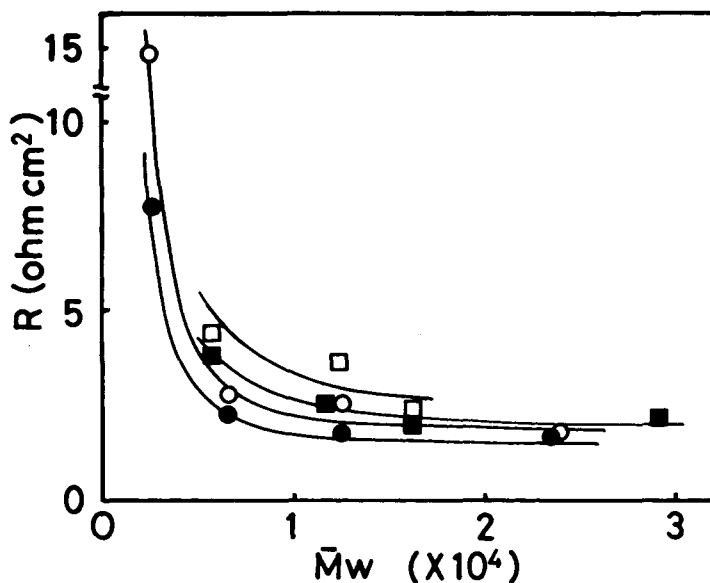


Fig. 13. Relationship between the electric resistance of the modified cationic exchange membrane and the molecular weight of the polymers as the modifier: ($-\circ-$) just after the modification by using the linear polymer; ($-\bullet-$) after the durability test by using the linear polymer; ($-\square-$) just after the modification by using the graft polymer; ($-\blacksquare-$) after the durability test by using the graft polymer. Linear polymer is poly(4-vinyl-*N*-methylpyridinium-iodide) and graft polymer is poly(benzyl)-*g*-poly(4-vinyl-*N*-methylpyridinium-iodide).

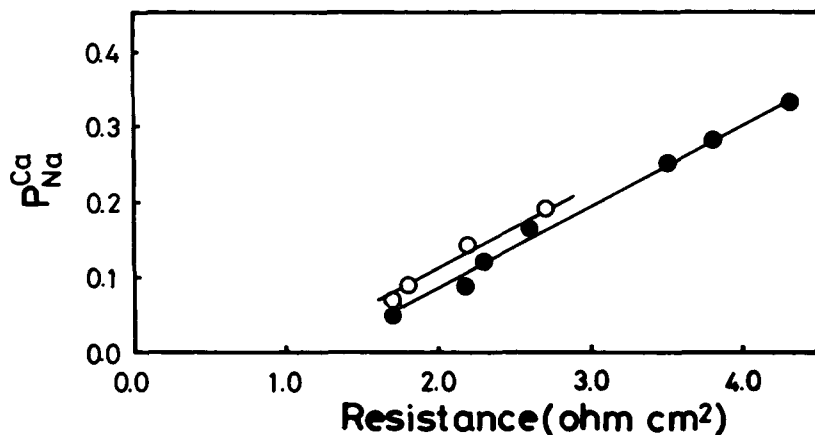


Fig. 14. Relationship between the electric resistances of the modified cation exchange membrane and P_{Na}^{Ca} in the current-passing method ($-\circ-$) poly(4-vinyl-*N*-methylpyridinium-iodide) ($-\bullet-$) poly(benzyl)-*g*-poly(4-vinyl-*N*-methylpyridinium-iodide).

groups, the thickness of the thin layer, the structure of the graft polymer, and the properties of the modified cation exchange membranes.

CONCLUSION

The effect of the poly(St-co-*p*-BSt)-graft-poly(4-vinyl-*N*-methylpyridinium-iodide) and poly(benzyl)-graft-poly(4-vinyl-*N*-methylpyridinium-

iodide) on the transport properties of the cation exchange membrane for the $\text{Na}^+ \text{-Ca}^{2+}$ system was studied and was compared with the poly(4-vinyl-*N*-methylpyridinium-iodide).

1. Both the polymers are more effective in membrane modification by the current-passing method.

2. In the case of membrane modification by the current-passing method, both polymers with the molecular weight of $10^4 \text{-} 2 \times 10^4$ are most effective.

3. In the case of the membrane modification by the current-passing method, $P_{\text{Na}}^{\text{Ca}}$ of the modified membrane becomes larger as the electric resistance becomes higher.

4. When the electric resistances are same, $P_{\text{Na}}^{\text{Ca}}$ of the membrane modified by the graft polymer is better than that by the linear polymer.

5. $P_{\text{Na}}^{\text{Ca}}$ and the durability of the membrane modified by both polymers are not as good as the membrane modified by the dipping method. On the other hand, both polymers are very effective in the membrane modified by the current-passing method.

Consequently, the cationic polyelectrolytes existing only on the surface of the membrane but not in the membrane are effective in obtaining good preferential permselectivity for the monovalent cation without any rise in the electric resistance of the membrane.

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