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Reverse Osmosis through Poly(4-Vinylpyridine-*co*-Methacrolein) Membranes Containing Functional Crosslinks of Complexing Ability

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Abstract

Membranes containing complex-formable crosslinks were obtained from poly(4-vinylpyridine-*co*-methacrolein) (4VL) when 4VL was crosslinked by the reaction of formyl groups of 4VL with malonyl dihydrazide (MD) or triethylene tetramine. The effect of monomer composition of 4VL, MD charged, and metal salts on the membrane performance in reverse osmotic separation of NaCl and $CoCl_2$ was investigated. The membranes of a high methacrolein content tended to be permselective, showing a maximal difference of about 60% in rejection between the two salts. 4VL membranes were mostly more permselective than poly(4-vinylpyridine-*co*-methyl vinyl ketone) membranes containing analogous crosslinks.

INTRODUCTION

Hydrophilic and functional groups of complexing ability are very useful for separation membranes and column resins. We have demonstrated that some membranes containing acylhydrazone in the backbone of the polycondensate of 2,5-pyridinedicarboxylic acid chloride and malonyl dihydrazide (MD) (*1*) and crosslinks obtained from poly(4-vinylpyridine-*co*-methyl vinyl ketone) (4VK) and MD (*2*) were selectively

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permeable to alkali metals and showed a potential capability of separating them from transition metals by complexing the latter with the membrane. Schiff base membranes derived from polyallylamine and salicylaldehyde and/or 2-pyridine carboxaldehyde also showed complex-forming ability and permselectivity when prepared under particular conditions (*3*). Polyallylamine originally has primary amino groups which have been used for Schiff base formation as well as crosslinking. Similarly, the starting polymers which contain formyl groups can form Schiff bases or hydrazones when they react with primary amines or hydrazines, respectively. Copolymers of acrolein or methacrolein fall in such a class of polymers. Since pyridine moieties also can complex with heavy metals (*4*) and contributed to the enhancement of flux and rejection of copolymer membranes (*5*), we have dealt with poly(4-vinylpyridine-*co*-methacrolein) (4VL) in this study. On crosslinking with a material containing two primary amino groups, 4VL could successfully be cast into fairly tough membranes. The present study is focused on the influence of the composition of 4VL, kind and quantity of crosslinking agents, and other casting conditions on the reverse osmotic performance of the copolymer membranes.

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EXPERIMENTAL

Copolymerization of 4-vinylpyridine (4VP, Wako Pure Chemicals Co., Japan) and methacrolein (ML, Tokyo Kasei Co., Japan) was carried out in an ampule in 30 wt% dimethylformaldehyde (DMF) solution with 2 mol% (based on total monomer) AIBN at 60°C for 30 h. The copolymer was precipitated in ethyl ether or water (4VL-3) and reprecipitated. The copolymer composition was determined by NMR in dimethylsulfoxide (DMSO)-d_6 (pyridine ring: δ8.4 (single, 2H), δ7.0–7.2 (single, 2H); CHO: δ5.0 (broad); CH_2 and CH of backbone: δ1.6 (broad), δ0.5 (broad)).

Membranes were prepared by casting on a glass plate 20 wt% DMSO solution containing 10–50 mol% crosslinking agent based on formyl groups of the copolymer, followed by drying at 80°C for a given time. The membranes were immersed in water overnight before use. They were about 40 μm thick.

Reverse osmosis was conducted with a batch-type apparatus and 0.06 *M* NaCl and $CoCl_2$ solution as a feed under a nitrogen pressure of 80 kg/cm^2 (7.85 MPa) at 25°C (*5*, *6*). The product concentration was determined by electric conductance measurement. Salt rejection R and hydraulic permeability K_1 were obtained from the following equations, respectively,

$$R = 100(c - c')/c$$

$$J_1 = K_1(\Delta p - \Delta\pi)/\Delta x$$

where c and c' are the feed and product concentrations, respectively; J_1 is the volumetric flux; Δp is the pressure difference; $\Delta\pi$ is the osmotic pressure difference between feed and product solution; and Δx is the membrane thickness.

Tensile strength, expressed as a value relative to the strength of cellulose acetate membrane (1180 g/mm^2) prepared by Manjikian's method (*7*), and water content in a wet membrane were estimated similarly as before (*1*, *5*).

Metal uptake capacity of the copolymers was determined by stripping the adsorbed metal ion with acid eluent followed by chelate-forming titration as described in a previous paper (*8*).

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RESULTS AND DISCUSSION

Preparation of Copolymers and Their Membranes

Radical copolymerization of ML has been carried out with acrylonitrile (*9*), methacrylonitrile (*10*), acrylamide (*11*), styrene (*12*), 1,2-dimethyl-5-vinyl-pyridinium methyl sulfate (*13*), and other monomers (*14*), but no attempt has been made to copolymerize with 4VP to our knowledge. The results of copolymerization are tabulated in Table 1. The increasing

TABLE 1
Copolymerization of 4-Vinylpyridine (4VP) and Methacrolein (ML)

Code	Molar ratio in monomer [4VP]/[ML]	Yield (%)	[4VP]/[ML] in copolymer	η_i[a]
4VL-3	70/30	87.2	74.0/26.0	0.140
4VL-1	50/50	77.1	48.7/51.3	0.118
4VL-4	50/50	78.3	48.6/51.4	0.113
4VL-2	20/80	71.6	23.2/76.8	0.102
4VL-6	10/90	60.5	13.2/86.8	0.056
PML	0/100	63.3	0/100	0.087

[a] Inherent viscosity of 0.5 wt% DMF solution at 25°C.

charge ratio of ML brought about a lower inherent viscosity, suggesting susceptibility of ML to chain transfer. In order to accomplish effective crosslinking upon preparing membranes, it was investigated for 4VL-1 and -2 whether gelation took place when their DMSO solution was heated at 80°C for 2 h with a primary amino groups-containing material; triethylene tetramine (TETA), 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl methane, malonyl dihydrazide (MD), and 2,5-pyridine dicarboxylic acid dihydrazide. TETA and MD readily gave rise to gelation, especially TETA in a few minutes even at room temperature, which often made it difficult to cast the polymer solution. Gelation of other substances brought small gel particles, but not to so great an extent of gelation as in TETA and MD. Therefore, the latter two substances were used as crosslinking agents. Particular stress was put on MD because MD readily gave tough membranes. That MD acts as an effective crosslinking agent has been demonstrated for 4VK (*2*). Membranes of 4VL-4 crosslinked with 30 mol% MD (based on ML) at drying times of 1.5 and 2 h showed R (%) against NaCl: 86.4 and 85.8; R against $CoCl_2$: 97.7 and 96.8, and $K_1 \times 10^9$ ($cm^2/s \cdot atm$) for NaCl: 1.08 and 1.03, $K_1 \times 10^9$ for $CoCl_2$: 1.04 and 0.88, respectively. Their relative strength and water content for 1.5 and 2 h drying were 1.7; 41% and 1.3; 59%, respectively. For the sake of comparison with the performance of reported membranes including 4VK (*2*), the drying time was determined to be 2 h.

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Effect of Crosslinking Agent

The dependence of the membrane performance on the charge ratio of MD is shown in Figs. 1 to 4. For 4VL-3 and -1 (Figs. 1 and 2) which contain ML of not more than about 50 mol%, it was possible to prepare membranes even with the addition of a stoichiometric amount of MD (50 mol% based on ML), and K_1 generally increased with an increasing amount of MD. At the same MD ratio, 4VL-3 had a K_1 value lower than taht of 4VL-1 which contained more ML and correspondingly a higher molar fraction of crosslinks. These facts represent the hydrophilic nature of the crosslink $-CH{=}NNHCOCH_2CONHN{=}CH-$. 4VL-3 showed high R values for both salts over a wide range of MD ratios (Fig. 1), while 4VL-1 had a maximal R at about 20–30 mol% MD. This fact indicates the contribution of 4VP to a high rejection in reverse osmosis, similarly as shown for poly(4VP-*co*-2,4-diamino-6-vinyl-*s*-triazine) (*15*). For 4VL-2 and -6 (Figs. 3 and 4) which contain ML higher than 50 mol%, addition of

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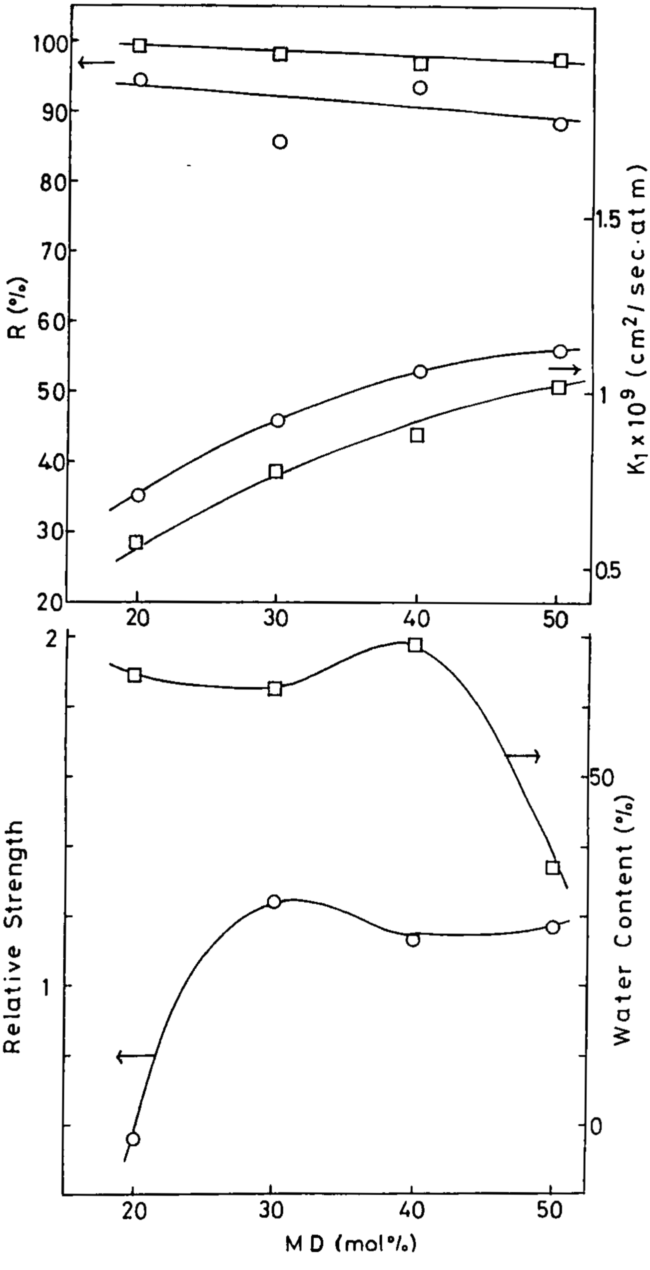

FIG. 1. Relationship between the performance and MD charged (based on ML) for 4VL-3 membranes ([4VP]/[ML] = 74.0/26.0). (○) NaCl feed, (□) $CoCl_2$ feed for R and K_1.

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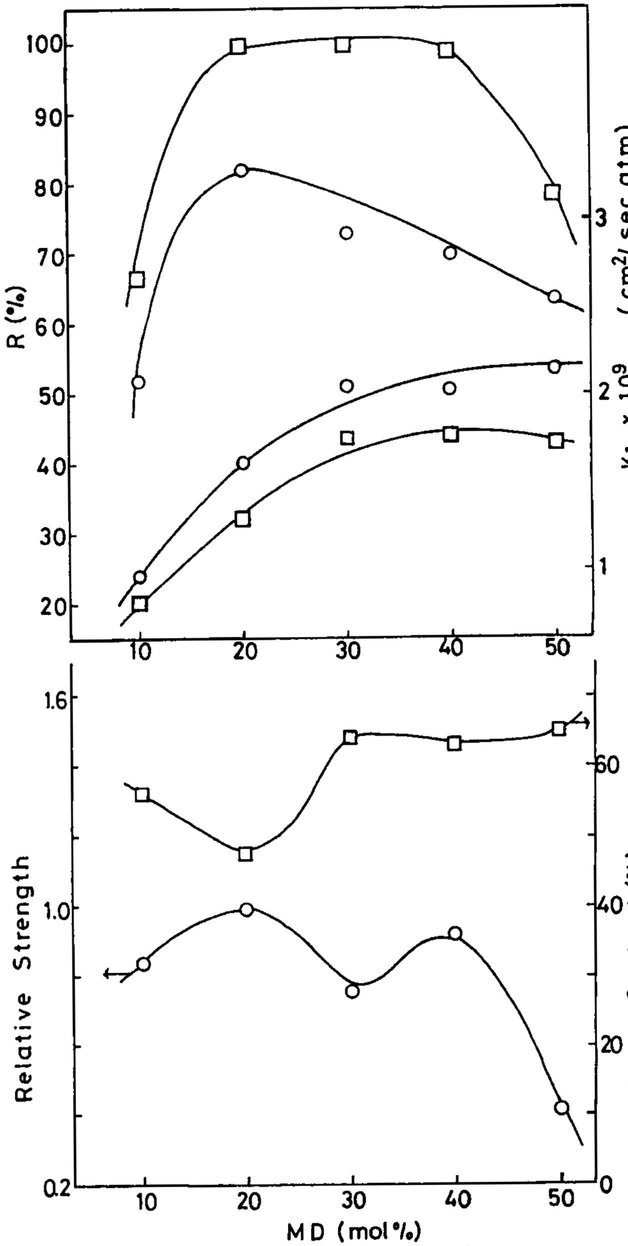

FIG. 2. Relationship between the performance and MD charged (based on ML) for 4VL-1 membranes ([4VP]/[ML] = 48.7/51.3). (O) NaCl feed, (□) $CoCl_2$ feed for *R* and K_1.

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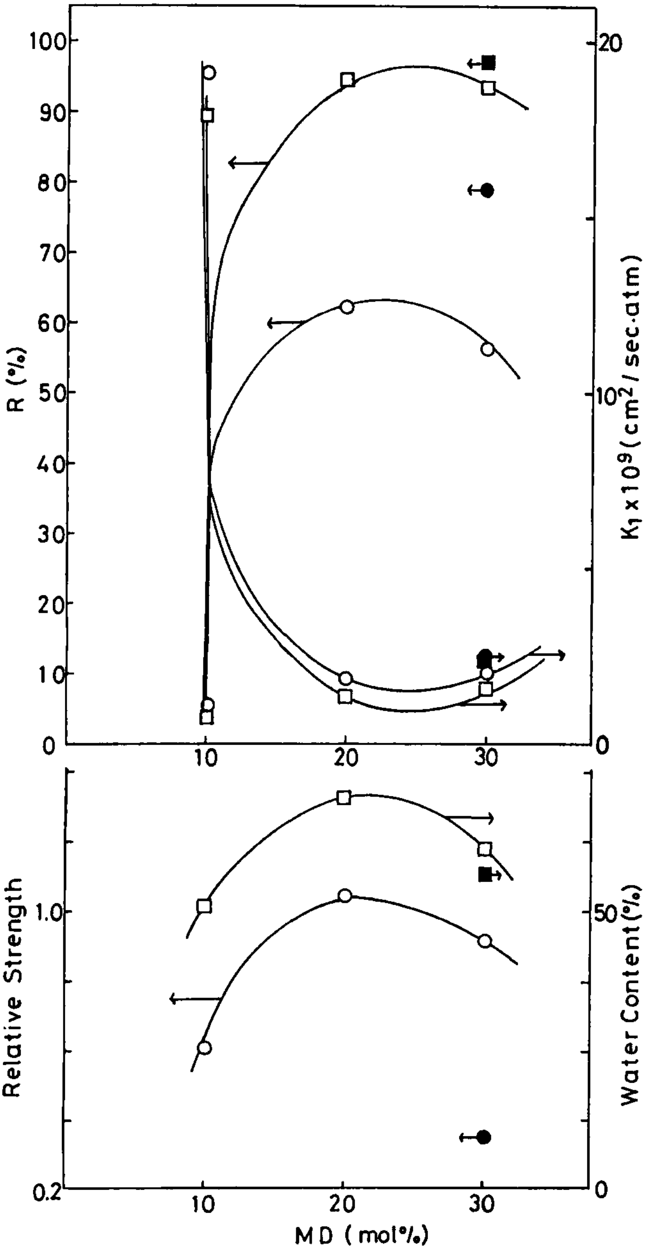

FIG. 3. Relationship between the performance and MD charged (based on ML) for 4VL-2 membranes ([4VP]/[ML] = 23.2/76.8). (○, ●) NaCl feed, (□, ■) $CoCl_2$ feed for *R* and K_1, (●, ■) crosslinked with TETA.

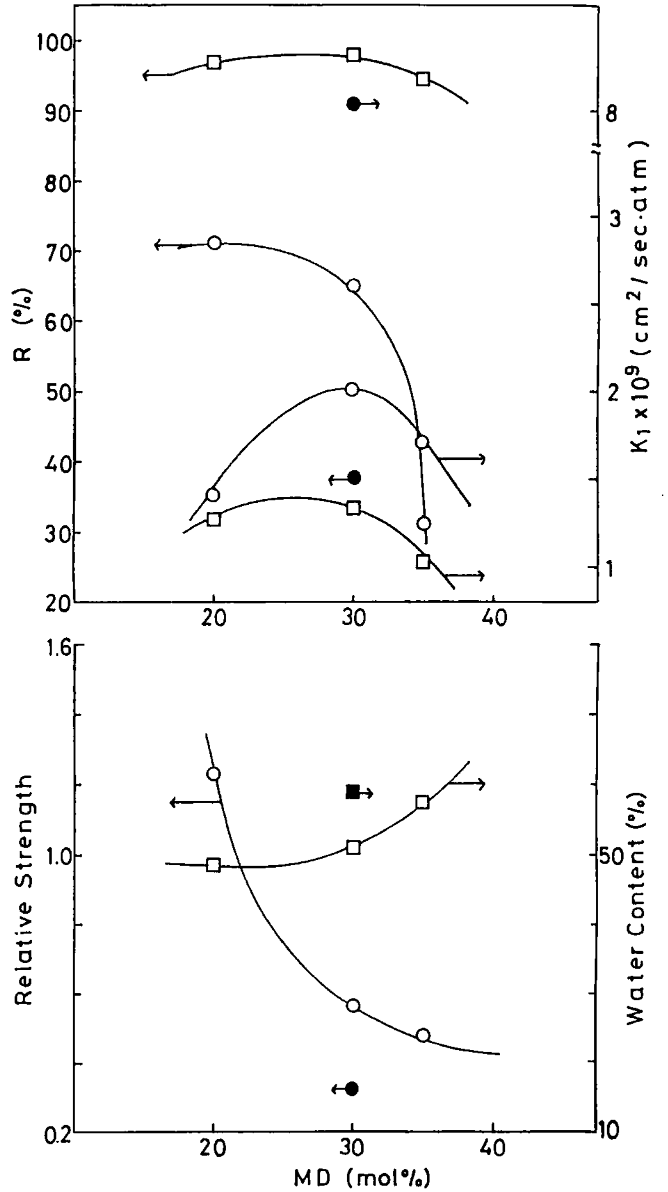

FIG. 4. Relationship between the performance and MD charged (based on ML) for 4VL-6 membranes ([4VP]/[ML] = 13.2/86.8). (○, ●) NaCl feed, (□) $CoCl_2$ feed for R and K_1, (●, ■) crosslinked with TETA.

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MD in a ratio higher than 35 mol% gave brittle or cracked membranes. This may be ascribed to an increase in pendent MD from polymer chains due to incomplete crosslinking which increases the distance between polymer chains, lowering the strength considerably. This is proved by the decreasing relative strength with increasing MD in Fig. 4. Very analogous results have been obtained in 4VK (*2*). Consequently, the adequate addition range of MD was concentrated to a range of about 15 mol% difference; from a value between 10 and 20 mol% to 30 mol% for 4VL-2 and from 20 to about 35 mol% for 4VL-6. Simultaneously, the difference in *R* between NaCl and $CoCl_2$ tended to become larger with an increase in MD, reaching about 60% at the addition of 35 mol% MD in Fig. 4. This permselectivity may be explained in terms of not only an improved capability of capturing Co^{2+} selectively by complexing with crosslink ligands, but also an enhanced permeability to Na^+ because of the inflexible and hard structure of the membrane due to dense crosslinking, leading to a more porous character, as is seen from the increasing water content in Fig. 4.

The relative strength of those membranes is generally around unity in Figs. 1 to 4, but about 20 mol% addition shows a tendency to give a membrane of higher strength. When TETA was used as a crosslinking agent, membrane preparation was often unsuccessful because prompt gelation occurred. Those membranes did not exhibit any characteristic performance which exceeded that of 4VL membranes, as is shown in Figs. 3 and 4.

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Effect of Copolymer Composition

The dependence of the performance on copolymer composition is illustrated in Figs. 5 and 6 by employing the same data shown in Figs. 1 to 4. As is seen in Fig. 5, high rejections against $CoCl_2$ were maintained throughout the whole composition employed in the range from 20 to 40 mol% MD. With increasing ML or decreasing 4VP, *R* against NaCl had a tendency to decrease, and the difference amounted to about 40% when 4VL containing 25 mol% ML (75 mol% 4VP) was charged with 30 mol% MD. In this study, however, a maximal difference of about 60% has been shown in Fig. 4 for 4VL-6 at the addition of 35 mol% MD. Figure 6 reveals that at 20 and 30 mol% addition of MD there was a composition range where a maximal K_1 was attained. The range was 50–75 mol% ML (50–25 mol% 4VP). In the charge ratio of 20–30 mol%, most of the added MD is considered to participate in the crosslinking reaction, resulting in an

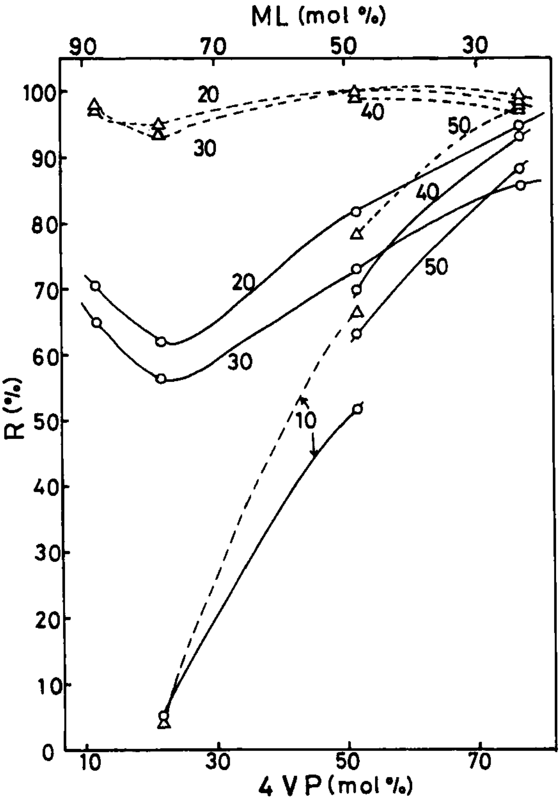

FIG. 5. *R* vs copolymer composition. (O) NaCl feed, (Δ) $CoCl_2$ feed. 10–50: MD charged (mol% based on ML).

improved performance. The copolymer composition close to a 1:1 molar ratio gave usable membranes over the widest range of MD, as shown in Fig. 2. This may be related to a monomer arrangement with an alternating tendency which would be favorable for retaining mechanical strength. A similar relationship has been observed between *R* and the composition of 4VK membranes (*2*).

Comparison with 4VK Membranes

The results of 4VL-1 (48.7 mol% 4VP, Fig. 2) may be compared with those of 4VK-8 (47.1 mol% 4VP) (*2*) that had a similar copolymer

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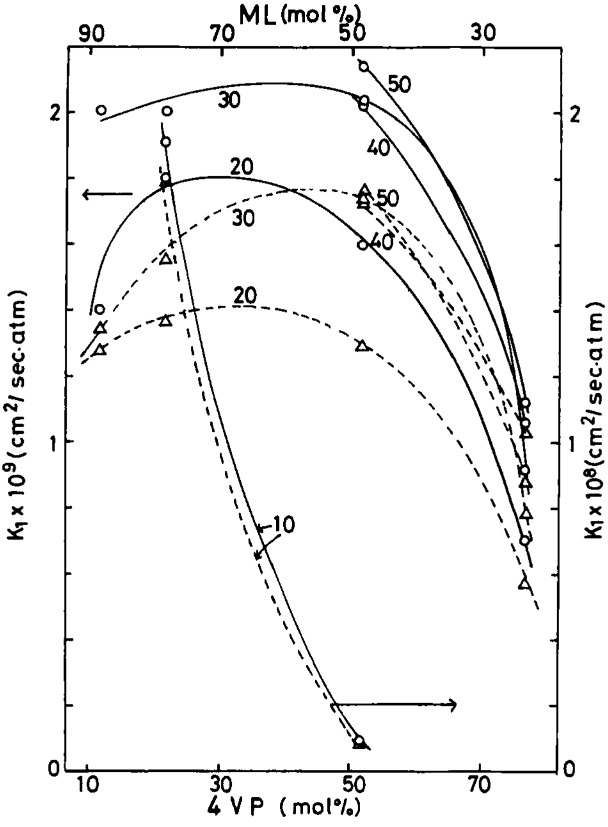

FIG. 6. K_1 vs copolymer composition. (O) NaCl feed. (△) $CoCl_2$ feed. 10–50: 10–50: MD charged (mol% based on ML).

composition and could form an analogous crosslink structure with MD. 4VK-8 membranes showed a maximal *R* at nearly 30 mol% MD. This resembles *R* against $CoCl_2$ in Fig. 2, but the *R* value of 4VK-8 was about 2% lower. *R* of 4VK-8 against NaCl, on the contrary, was a few percent higher. K_1 values of 4VL-1 membranes at 30 mol% MD are about 3 times higher. Therefore, at the addition of 30 mol% MD, 4VL membranes are more permselective and more water permeable than 4VK membranes of the corresponding copolymer composition, in spite of a lower degree of polymerization in 4VL (intrisnic viscosity of 4VKs was about 0.35 (*2*)) and lower relative strength of 4VL-1 membrane (0.8–1.0) in comparison with that of 4VK-8 (1.2–1.3). As for the influence of copolymer composition on

R and K_1, 4VK showed a maximal *R* and minimal K_1 at about 50 mol% 4VP (*2*). This is quite different from Fig. 5, which again represents the permselective character of 4VL membranes.

Potential Rejection of Other Metal Salts

Since $CoCl_2$ is rejected by complex formation with ligands in the membrane matrix, other transition or heavy metal salts may be rejected in a similar manner. Membranes of 4VK oxime showed a tendency to reject more readily the metal salt which was taken up in a larger amount (*5*). Therefore, the metal uptake for MD-crosslinked 4VL-4 was examined with several metal salts. Table 2 summarizes the results. $CoCl_2$ showed the least uptake among the metal salts used, suggesting that metal salts other than $CoCl_2$ can be more easily rejected in reverse osmosis. It has been demonstrated that membranes derived from the amidoxime of poly(4VP-*co*-acrylonitrile) effectively reject those salts (*8*).

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CONCLUSION

Of the primary amino groups-containing substances examined, MD was the most appropriate crosslinking agent for the reverse osmosis membranes prepared from 4VL. The range where a membrane was successfully prepared can be summarized from Fig. 7. The membrane comprised of 4VL containing 50–75 mol% ML and crosslinked with 20–30 mol% MD based on ML showed good membrane performance. A membrane with a higher ML content had a tendency to show a larger difference in *R* between NaCl and $CoCl_2$ feed, and 4VL containing about 90 mol% ML afforded a permselective membrane which exhibited a maximal difference of about 60%. 4VL membranes crosslinked with MD were generally more permselective than 4VK membranes. It is suggested

TABLE 2

Metal Uptake by 4VL-4[a]

Metal salt	$CuCl_2$	$Cu(NO_3)_2$	$CoCl_2$	$NiCl_2$	$ZnCl_2$	$Hg(OAc)_2$[b]
Uptake (meq/g)	0.96	0.85	0.27	0.61	0.83	4.47

[a] Heated with 50 mol% MD based on ML in DMSO at 80°C for 2 h and pulverized (200 mesh). Buffer: HCl-AcONa at pH 5. Eluent: 1 *N* HCl.

[b] Buffer: AcOH-AcONa at pH 5. Eluent: 1 *N* HNO_3.

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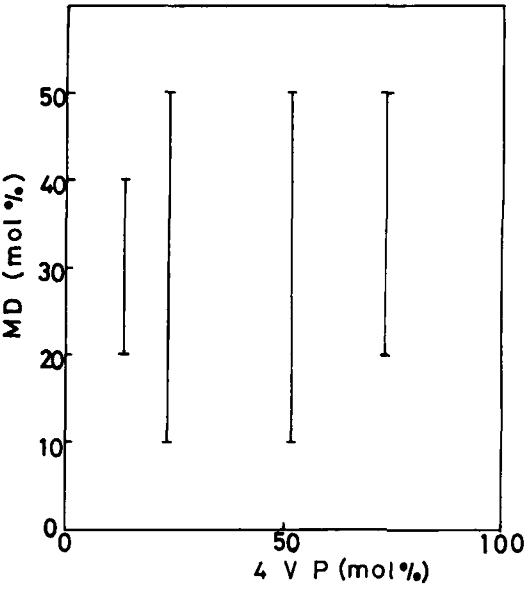

FIG. 7. The range of MD charged and the composition where membranes could be obtained.

that those 4VL membranes effectively reject transition metal salts other than $CoCl_2$ as well.

REFERENCES

1. E. Oikawa and K. Jindai, *Polym. Bull., 16,* 351 (1986).
2. E. Oikawa and Y. Igarashi, *J. Appl. Polym. Sci., 29,* 1723 (1984).
3. E. Oikawa and K. Yahata, *Polym. Bull., 17,* 315 (1987).
4. N. H. Agnew, *J. Polym. Sci., Polym. Chem. Ed., 14,* 2819 (1976).
5. E. Oikawa, Y. Igarashi, and S. Tsurumaki, *J. Appl. Polym. Sci., 30,* 1511 (1985).
6. E. Oikawa and T. Ohsaki, *Desalination, 25,* 187 (1978).
7. S. Manjikian and C. Allen, *Research and Development Progress Report No. 378,* Office of Saline Water, 1968.
8. E. Oikawa and S. Tsurumaki, *J. Appl. Polym. Sci., 34,* 337 (1987).
9. H. C. Haas and M. S. Simon, *J. Polym. Sci., 9,* 309 (1952); A. R. Kol'k, A. A. Konkin, and Z. A. Rogovin, *Khim. Volokna,* (4), 12 (1963).
10. R. C. Schulz, E. Kaiser, and W. Kern, *Makromol. Chem., 58,* 160 (1962).
11. F. S. Dainton and W. D. Sisley, *Trans. Faraday Soc., 59,* 1385 (1963).
12. W. E. Smith, G. E. Ham, H. D. Anspon, S. E. Gebura, and D. W. Alwani, *J. Polym. Sci., Part A-1, 6,* 2001 (1968); O. Seycek, B. Bednar, M. Houska, and J. Kalal, *Collect. Czech. Chem. Commun., 47,* 785 (1982).

13. W. P. Shyluk, *J. Polym. Sci., A2,* 2191 (1964).

14. L. Ambroz, J. Caskova, M. Jelinek, J. Milan, J. Majer, and V. Pidrova, *Chem. Prum., 26,* 27, 82 (1976).

15. E. Oikawa and Y. Honda, *Kobunshi Ronbunshu, 39,* 571 (1982).

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