

Properties of Poly(4-vinylpyridine-Co-Methyl Vinyl Ketone) Membranes for Reverse Osmosis

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Synopsis

The copolymer prepared from 4-vinylpyridine and methyl vinyl ketone could form a dense and tough membrane which is stronger than cellulose acetate when crosslinked with malonyl dihydrazide (MD) or 2-phenyl-4,6-dihydrazino-*s*-triazine (PDT), showing a fair performance in reverse osmosis for NaCl and CoCl₂ feed. The relationship between the content of MD or PDT and the membrane performance was investigated. An increase in MD or PDT led to an increase in membrane thickness and water content as well as the performance. A maximum rejection was obtained at ca. 30 mol % MD and ca. 13 mol % PDT based on MVK, and a maximum membrane strength at 20–30 mol % crosslinking agent. A membrane of a lower NaCl rejection tended to be permselective due to the complexation of the CoCl₂ with membrane. About 1:1 copolymer gave membranes of a higher rejection, which may be related to monomer arrangement in the copolymer chain. Three methods for the flux improvement were presented and discussed: preparation of a copolymer blend membrane containing a hydrophilic monomer, crosslinking quaternization of membranes with diiodobutane, and oximation of the membrane material in order to introduce hydrophilic groups.

INTRODUCTION

In our previous paper we have dealt with reverse osmotic properties of copolymer membranes prepared from a monomer in common use, particularly 4-vinylpyridine (4VP) and a comonomer such as acrylonitrile,^{1,2} vinylidene chloride,³ and 2,4-diamino-6-vinyl-*s*-triazine (DAVT).^{4,5} In the latter copolymer it was found that cobalt- or copper-salt-complexed membranes improved salt rejection without flux decrease.⁶ This is a quite different behavior from that of cellulose acetate membranes containing an inorganic salt such as magnesium perchlorate or lithium nitrate in casting. The rejection enhancement in the complexed membranes may be accounted for by the conversion of the membrane character into a polar or charged one due to the formation of coordinated bonds between a transition metal salt and pyridine rings.⁵ Therefore, if the comonomer is able to form a complex in a manner similar to 4VP, the copolymer would be a stronger ligand in complexing with a transition metal salt, resulting in a much higher salt rejection. Since a carbonyl derivative is a weak ligand and carbonyl group can be converted to a form or group of complexing or chelating ability, such as β -diketone, Schiff base, hydrazine, oxime, and so on, we have made an attempt in this paper to prepare the copolymer of methyl vinyl ketone (MVK) with 4VP and introduce some of the above functional structures to the copolymer or modify it by other chemical means, thus yielding the copolymer membranes of high performance in reverse osmosis.

EXPERIMENTAL

Materials. The monomers and solvents were distilled before use. Commercially available malonyl dihydrazide (MD) was recrystallized from ethanol. 2-Phenyl-4,6-dihydrazino-*s*-triazine (PDT) was prepared from 2-phenyl-4,6-dichloro-*s*-triazine and hydrazine hydrate.⁷ 1,4-Diiodobutane (DIB) was prepared from tetrahydrofuran, potassium iodide, and phosphoric acid.⁸

Copolymerization. A required amount of 4VP and MVK were copolymerized in a nitrogen atmosphere under the conditions described in Table I. The copolymers were purified by reprecipitation from methanol or *N,N*-dimethylformamide (DMF) solution into diethyl ether.

Copolymerization of 4VP with acrylamide (AAM), 4VP with *N*-vinyl-2-pyrrolidinone (NVP) (in DMF medium), and terpolymerization of these three monomers were carried out in a similar fashion.

Copolymer composition was determined by comparison of the area at $\delta 6.6$ and $\delta 8.4$ due to pyridine rings with that at $\delta 1.7$ – 2.5 due to methyl and methylene groups in NMR spectra.

Oximation of Copolymer. In a 500-mL three-necked flask, 15 g of 4VK8 was dissolved in 300 mL of absolute ethanol, and 15 g of hydroxylamine hydrochloride and 30 g of anhydrous sodium acetate were added. The mixture was refluxed with mechanical stirring for 5 h. The reaction mixture was poured into acetone. The precipitate was filtered and dissolved in DMF. The solution was filtered through cellite (ca. 1 cm thick) on a filter in order to remove inorganic impurity and again poured into acetone. This was repeated. The yield was 12.8 g (79.7%). The conversion of C=O to C=NOH was estimated to be 98.9% from elemental analysis.

Membrane Preparation. The copolymer membranes were prepared from 25 wt % dimethyl sulfoxide (DMSO) or DMF solution similarly as in a previous publication.⁶ In the preparation of cobaltous chloride (CoCl₂)-charged membranes a required amount of 2 wt % DMF solution of CoCl₂ was added to the casting solution, and the mixture was then heated with magnetic stirring until it became homogeneous, and cast. The thickness of the membranes thus formed ranged from 40 to 100 μm in a wet state.

Some of the membranes were subjected to heat treatment in hot water or 2 wt % CoCl₂ solution at 80°C for 10 min.

Reverse Osmosis. The apparatus and experimental procedures were similar as described in previous papers.^{2,6} Nitrogen pressure of 80 kg/cm² was applied at 25°C. The salt concentration of feed solutions was 0.06M. The product concentration was determined by Mohr's method for sodium chloride (NaCl) and by electric conductance measurements for CoCl₂. Salt rejection R and hydraulic water permeability K_1 were obtained from the following equations, respectively:

$$R = 100(c - c')/c \quad (1)$$

$$J_v = K_1(\Delta P - \Delta\pi)/\Delta x \quad (2)$$

where c and c' are feed and product concentration, respectively, J_v is volumetric flux, ΔP pressure difference, $\Delta\pi$ osmotic pressure difference between feed and product solution, and Δx membrane thickness.

TABLE I
Copolymerization of 4-Vinylpyridine with Methyl Vinyl Ketone^a

Code no.	4VP charged (mol %)	Yield (%)	4VP in copolymer ^b (mol %)	$[\eta]^c$
4VK7	30	69.3	33.2	0.36
4VK9	40	71.1	40.5	0.35
4VK3	50	71.3	47.4	0.34
4VK5	50	72.2	48.3	0.31
4VK8	50	71.5	47.1	0.33
4VK10	50	73.7	46.5	0.38
4VK11	60	74.9	54.7	0.33
4VK6	70	74.8	64.6	0.36

^a Monomers: 40 wt % in dioxane; azobisisobutyronitrile: 0.25 mol % based on monomers; 80°C, 6 h; precipitant: diethyl ether.

^b Determined by NMR.

^c In DMF at 25°C.

The measurements of NMR, water content, and relative tensile strength which is defined as tensile strength of the copolymer membranes divided by that of cellulose acetate membrane prepared by Manjikian's method⁹ were conducted in the same manner as described previously.^{2,3}

RESULTS AND DISCUSSION

Membrane Preparation. The results of the copolymerization were tabulated in Table I. Alternating tendency in the monomer arrangement was observed when copolymer composition was compared with monomer charge ratio. The yields and intrinsic viscosities were very similar to each other irrespective of the charge ratio.

The copolymer membrane was soft, rubbery, and rather sticky, and had to be strengthened by crosslinking. An attempt was made to form Schiff base crosslinks by employing 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenyl ether, or ethylenediamine, but any adequate strength against the applied pressure was not obtained. Aldol condensation was not successful either. However, a dihydrazine derivative which gives hydrazone crosslinks produced readily tough

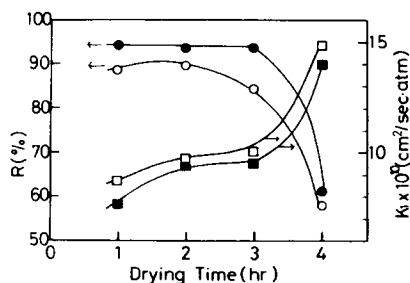


Fig. 1. R and K_1 vs. drying time for 4VK11 membranes cast from DMSO solution charged with 35 mol % MD based on MVK: (○, □) NaCl feed; (●, ■) CoCl₂ feed.

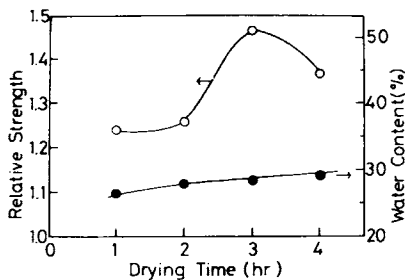


Fig. 2. Relative strength and water content vs. drying time for the same membranes as in Figure 1.

membranes. Therefore, in the first place the influence of drying time on the performance of MD-crosslinked membrane was checked at the copolymer concentration of 25 wt % and at 80°C as is shown in Figures 1 and 2. Three hours appeared most appropriate for maximum strength and rejection, but NaCl rejection decreased, probably due to membrane faults caused by a longer drying period. Hence, the membranes were prepared by drying for 2 h throughout this study unless otherwise noted.

Effect of Crosslinking Agent. The effect of MD and PDT content on the membrane performance was investigated. The results are illustrated in Figures 3–6. PDT was less soluble in DMSO than MD, so that a higher concentration of PDT could not be realized. R increased with increasing MD or PDT content toward a maximum at about 30 mol % for MD in Figure 3 and 13 mol % for PDT in Figure 4 and then decreased rapidly, especially in NaCl feed, whereas K_1 increased continuously. The increase in K_1 may indicate that hydrazone or hydrazide groups as well as *s*-triazine rings are hydrophilic. That the *s*-triazine ring is hydrophilic has been demonstrated previously.⁵ Comparison of K_1 and

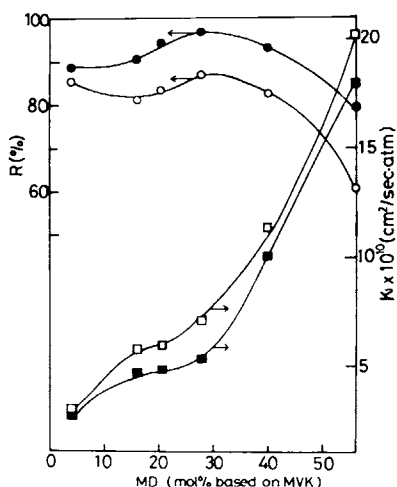


Fig. 3. R and K_1 vs. MD charged for 4VK8 membranes cast from DMSO solution; cf. Figure 1 for symbols.

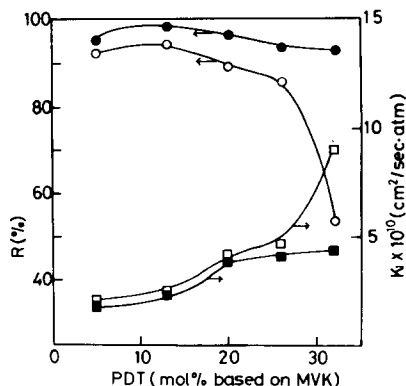


Fig. 4. R and K_1 vs. PDT charged for 4VK10 membranes cast from DMSO solution; cf. Figure 1 for symbols.

water content for MD in Figures 3 and 5 with those for PDT in Figures 4 and 6 reveals that MD is more hydrophilic and gives a membrane containing more water. The membranes thus formed had a maximum relative strength of 1.29 for MD and 1.66 for PDT in the range of 20–30 mol % and characterized by a higher strength than that of cellulose acetate.

Charging a larger amount of MD or PDT gave a membrane of a decreased R and strength. This can be ascribed to an increase in pendent MD or PDT from polymer chains due to incomplete crosslinking, which gives rise to an increase in the distance between polymer chains and in pores of molecular size. This can be more appreciable for PDT because of its bulky structure, as is shown by a marked reduction of R for NaCl feed at more than 25 mol % charge (Fig. 4) in comparison with MD (Fig. 3). However, the membrane charged with 30 mol % PDT was permselective, showing a considerable difference between R 's of NaCl

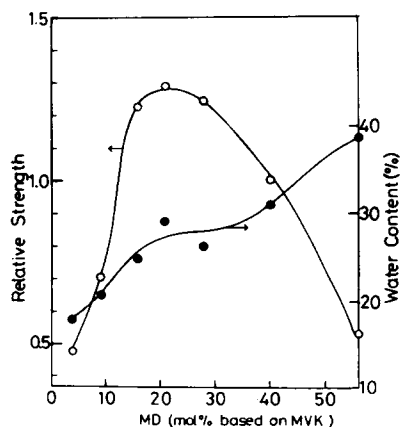


Fig. 5. Relative strength and water content vs. MD charged for the same membranes as in Figure 3.

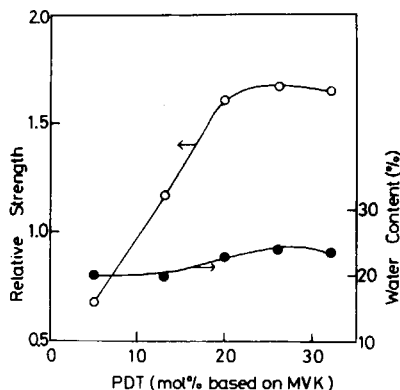


Fig. 6. Relative strength and water content vs. PDT charged for the same membranes as in Figure 4.

and CoCl_2 , and, therefore, such a membrane seems to be useful for the separation of the two metals. The large difference in R may be accounted for by not only the difference in atomic size and valence but also the rejection of the same ions by CoCl_2 that is complexed with membrane material.

The membrane thickness which was measured prior to the application of pressure increased along with MD or PDT charged, as shown in Figure 7. Since all the membranes prepared in the present study were transparent and could be regarded as dense membranes, salt rejection per unit thickness was plotted against mol % MD or PDT in Figure 7. The results show a decrease in R per unit thickness with an increase in MD or PDT. This fact and the increase in K_1 in Figures 3 and 4 indicate that the addition of MD or PDT brings about an increase in pores and that the initial enhancement of R in Figures 3 and 4 is caused to a large extent by an increment of the membrane thickness. The bound water may

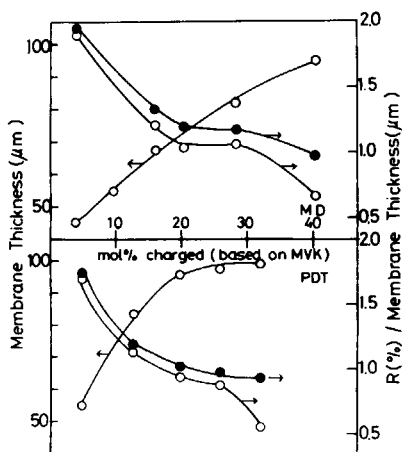


Fig. 7. Membrane thickness and rejection over membrane thickness vs. MD or PDT charged for the same membranes as in Figures 3 and 4, respectively; cf. Figure 1 for symbols of the right ordinate.

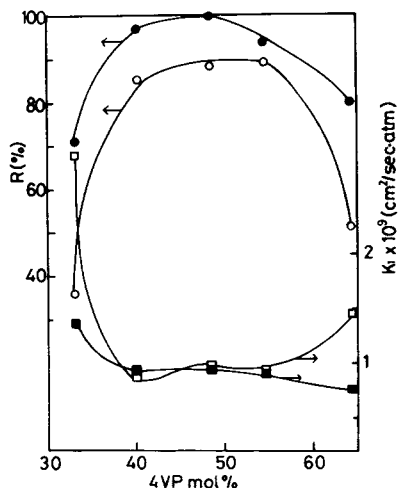


Fig. 8. R and K_1 vs. copolymer composition. Cast from DMSO solution charged with 35 mol % MD; cf. Figure 1 for symbols.

increase as well with the increase in the water content and contribute to the improvement of R .

Dependence on Copolymer Composition. Figure 8 shows the dependence of R and K_1 on copolymer composition. MD charged was kept constant at 35 mol % based on MVK, where R would remain around the maximum value. However, the weight ratio of MD to the copolymer is always different depending on the copolymer composition. In Figure 9, therefore, the weight ratio was kept constant at 15 wt %, probably giving a crosslinking degree similar to each other. Since 35 mol % MD for 4VK6 (64.6 mol % 4VP) exactly corresponds to 15 wt % MD, other copolymers consisting of a larger amount of MVK contain less than 35 mol % MD.

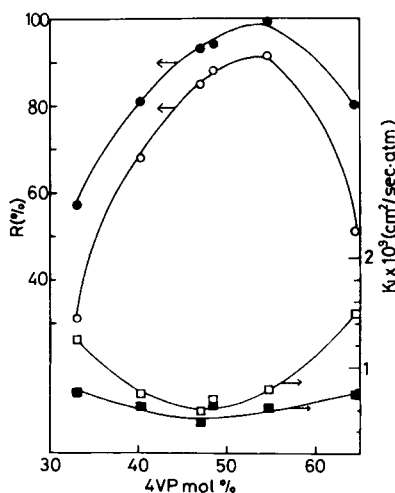


Fig. 9. R and K_1 vs. copolymer composition. Cast from DMSO solution charged with 15 wt % MD; cf. Figure 1 for symbols.

TABLE II
Performance of CoCl_2 -Charged Membranes^a for NaCl Feed

Mol % CoCl_2 charged based on 4VP	0	2	3	4
R (%)	77.8 (91.0)	80.6	83.2	82.2 (93.2)
$K_1 \times 10^{10}$ ($\text{cm}^2/\text{s}\cdot\text{atm}$)	2.54 (1.98)	3.42	3.05	2.80 (2.41)
Relative strength	0.67	0.59	0.92	0.74
Water content (%)	25.1	25.7	25.1	26.8

^a Cast from DMF solution of 4VK5 charged with 5 mol % PDT. Numbers in parentheses indicate the results for CoCl_2 feed.

It is seen in Figures 8 and 9 that the copolymer of 50–55 mol % 4VP showed a maximum of R . This can be related to the monomer arrangement of alternating tendency which would favor a dense packing of the copolymer chains in the membrane structure.

The relative tensile strength of 35 mol % charged membranes and 15 wt % charged membranes ranged from 1.0 to 1.22 and from 1.17 to 1.33, respectively, and was again prone to reach a maximum around 50 mol % 4VP. This tendency is also related to the membrane structure. In the former membranes water content did not change appreciably ranging from 29.3% to 31.6% and in the latter membranes it gradually increased from 24.9% to 31.0%.

In summary a copolymer composition of 50–55 mol % 4VP is favorable for the salt separation.

Complexation of CoCl_2 prior to Reverse Osmosis. In our previous study the CoCl_2 complexed 4VP–DAVT copolymer membranes have increased R and strength without a decrease in K_1 in the range of about 5 mol % CoCl_2 based on 4VP.⁶ A similar behavior was expected in the 4VK copolymer membranes. The membranes prepared from 4VK by the addition of CoCl_2 alone were soft and could not be used for reverse osmosis. Hence, 5 mol % PDT was charged in addition to CoCl_2 . The performance of the resultant membranes was summarized in Table II. As can be seen from Table II, CoCl_2 -charged membranes could

TABLE III
Performance of Hot-Water- or CoCl_2 -Solution-Treated^a Membrane^b for NaCl Feed

	Untreated	Treated in water	Treated in 2 wt % CoCl_2 solution
R (%)	77.8 (94.2)	94.3 (98.4)	90.9 (99.0)
$K_1 \times 10^{10}$ ($\text{cm}^2/\text{s}\cdot\text{atm}$)	8.02 (6.46)	7.24 (7.10)	6.52 (5.87)
Relative strength	0.91	1.04	1.09
Water content (%)	29.8	27.8	27.1
Contraction in length (%)	—	0.47	1.00

^a At 80°C for 10 min.

^b Cast from DMSO solution of 4VK6 charged with 35 mol % MD and dried for 1 h. Numbers in parentheses indicate the results for CoCl_2 feed.

TABLE IV
 Performance of Terpolymer Membranes^a

	4VK3	4VKA ^b	4VKP ^c
<i>R</i> (%)	85.4 (96.2)	92.0 (99.2)	78.8 (90.0)
$K_1 \times 10^{10}$ (cm ² /s-atm)	2.10 (1.86)	2.02 (1.96)	2.86 (2.69)
Relative strength	0.63	0.68	0.52
Water content (%)	15.4	20.8	21.3

^a Cast from DMF solution charged with 5 mol % PDT. Numbers in parentheses indicate the results for CoCl₂ feed.

^b 43 mol % 4VP, 44 mol % MVK, 13 mol % AAM.

^c 42 mol % 4VP, 49 mol % MVK, 9 mol % NVP.

slightly increase *R* without a decrease in K_1 , but not so remarkably as demonstrated in 4VP-DAVT copolymer membranes.⁶ This is because CoCl₂ forms a complex with PDT, which interrupts the complexation with pyridine rings of the copolymer. The complexation of CoCl₂ with PDT was proved by the instantaneous color change to green when blue DMF solution of CoCl₂ was added to colorless PDT solution.

As an alternate way of complexation, only the surfaces of a crosslinked membrane prepared in advance was complexed in CoCl₂ solution, as was evidenced by the coloration of the membrane. The results are tabulated in Table III together with those of untreated and hot-water-treated membranes. Both the hot-water-treated and CoCl₂-solution-treated membranes showed higher *R* values than the untreated membranes, but there was no substantial difference observed between the two treated membranes. It is apparent from these results that the effect of membrane contraction, though it was small, surpasses the effect of the metal salt complexation.

Improvement of Water Permeability. The membranes obtained in the

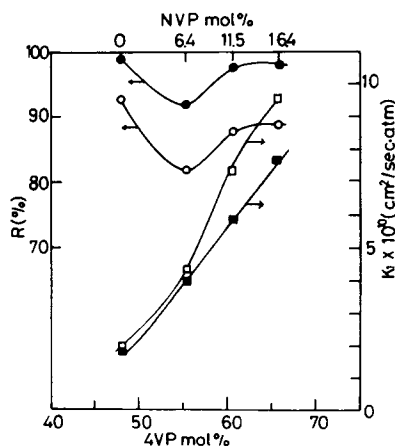


Fig. 10. *R* and K_1 vs. composition of copolymer blend membrane of 4VP-NVP (26.3 mol % NVP) and 4VK5 cast from DMF solution charged with 2.6 wt % PDT; cf. Figure 1 for symbols.

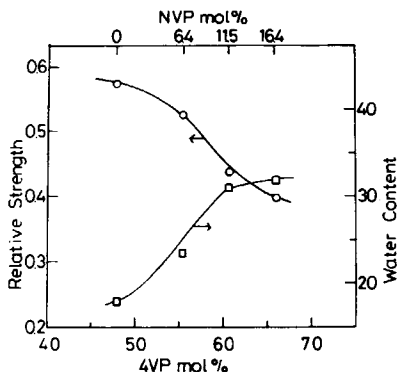


Fig. 11. Relative strength and water content vs. composition of the same copolymer blend membrane as in Figure 10.

present study by crosslinking with MD or PDT showed a high salt rejection of 99.6% for CoCl_2 in Figure 9 and 94.2% for NaCl in Figure 4. Water flux at best, on the other hand, is about $22 \text{ l/m}^2\text{-day}$ when K_1 is $2 \times 10^{-9} \text{ cm}^2/\text{s-atm}$ and thickness is $60 \mu\text{m}$ according to eq. (2). The flux was markedly improved by crosslinking with MD or PDT, but was not large when compared with that of commercial membranes; further enhancement of the flux is desirable.

The following three attempts were made in order to improve the water flux:

(a) *Introduction of a hydrophilic monomer into the 4VK copolymer.* In the first place terpolymers were prepared including AAM or NVP. The performance of the terpolymers was tabulated in Table IV. 4VKP improved K_1 to some extent but was accompanied by a decrease in R . 4VKA reduced K_1 while R was increased. Thus, terpolymerization does not seem to become a powerful means

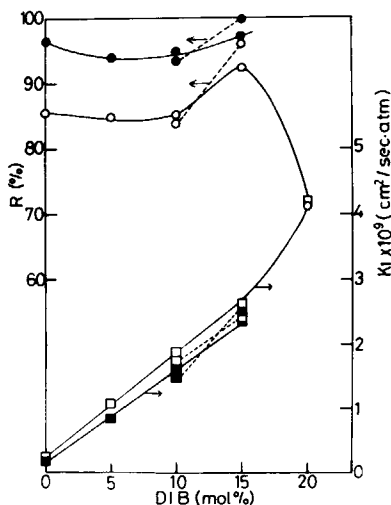


Fig. 12. R and K_1 vs. DIB charged based on 4VP content for 4VK3 membranes cast from DMF solution charged with 5 mol % PDT: (---) heated in hot water at 80°C for 10 min. Cf. Figure 1 for symbols.

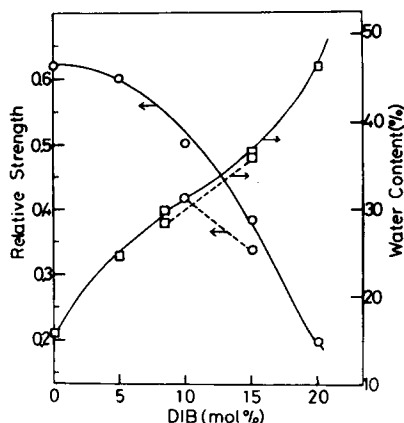


Fig. 13. Relative strength and water content vs. DIB charged for the same membranes as in Figure 12. (---) the same treatment as in Figure 12.

for the flux improvement. A second attempt was the preparation of copolymer blend membranes from a DMF solution containing 2.6 wt % PDT. Two copolymer blends were used, i.e., a blend of 4VP-AAM copolymer (54.2 mol % AAM) and 4VK5, and that of 4VP-NVP copolymer (26.3 mol % NVP) and 4VK5. The former blend did not form a homogeneous mixture nor did it give a uniform membrane. The latter copolymers, on the other hand, were compatible, and membranes of their blends showed a comparable performance, as illustrated in Figures 10 and 11, where the curves depict the effects of the 4VP and NVP contents in the blend. The blend membrane containing 16.4 mol % NVP had higher values of R and K_1 than those for some of the membranes in Figure 9. The R values of the same blend membrane were larger than those for 4VK6 (64.6 mol % 4VP) in Figure 9, which had a similar content of 4VP, though K_1 values were comparable. Apparently, K_1 increased four to five times with increasing NVP and 4VP contents (Fig. 10) whereas the relative strength decreased (Fig. 11). The addition of a larger amount of PDT or an other crosslinking agent may reinforce the membrane.

(b) *Conversion to a charged membrane with DIB.* It has been demonstrated that the DIB-quaternized and -crosslinked 4VP copolymer membranes showed an improved performance, especially with less 4VP containing copolymers.²⁻⁴ The effect of DIB was investigated in the present study as well. The results are shown in Figures 12 and 13. R had a maximum at 15 mol % DIB, though it was slightly reduced at 5 and 10 mol % DIB, whereas K_1 linearly increased with DIB content. It is seen from these results that R and K_1 were best improved at 15 mol % DIB and further enhanced by the hot water treatment. Although of lower strength, the membranes were still able to be used at the applied pressure. Thus, with a dilute feed solution, the crosslinking quaternization with an α,ω -dihalogenated compound is very effective for the flux improvement.

(c) *Other chemical modification of the copolymers.* The modification involves all the chemical reactions which convert a part of the copolymer into hydrophilic moiety. From many reactions which can bring hydrophilic groups to the copolymer was chosen the introduction of hydroxyl groups by oximation with hydroxylamine. The oximation was readily accomplished, and the oximated copolymer of 4VK8, for example, could be successfully used for membrane

preparation with divinyl sulfone as a crosslinking agent, whose reaction involves hydrogen transfer. The membranes thus formed were tougher than a cellulose acetate membrane and could be charged with up to 40 mol % DIB. The performance at 15 mol % DIB was superior in all respects to that of 4VK3 membranes used in Figures 12 and 13: R , 95.1% (NaCl), 99.4% (CoCl₂); K_1 , 2.8×10^{-9} (NaCl), 2.7×10^{-9} (CoCl₂); relative strength, 0.72.

The detailed characteristics of the membranes of the oximated 4VK copolymers will appear in a future publication.

CONCLUSIONS

Although the membranes from poly4VP and polyMVK were too soft and weak to be used for reverse osmosis, 4VP-MVK copolymers crosslinked with a dihydrazine derivative MD or PDT yielded dense and tough membranes. The addition of MD or PDT increased membrane thickness, water permeability, and water content. An appropriate charge ratio for an effective separation was found: ca. 30 mol % for MD and ca. 13 mol % for PDT. In a wide range of the charge ratio, CoCl₂ was rejected effectively through complexation with the membrane.

The membrane was 1.3–1.7 times stronger than cellulose acetate membrane at 20–30 mol % MD or PDT.

About 1:1 copolymer gave a membrane of a maximum rejection, which is probably related to membrane structure resulting from the monomer arrangement of alternating tendency.

A more hydrophilic MD was preferable to PDT for the enhancement of K_1 . NVP-containing copolymer blends have a potential for the improvement of K_1 , provided that the membranes are reinforced.

Since DIB-quaternized membranes remarkably improved K_1 , this procedure is useful for a dilute feed.

The 4VK copolymer which was chemically modified for introducing a hydrophilic group has some prospects, as exemplified by oximation, for the improvement of the membrane performance.

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Received July 22, 1983

Accepted October 12, 1983