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The Characteristics of Cobalt or Copper Salt-Coordinated Poly(4-Vinylpyridine-co-2,4-Diamino-6-Vinyl-s-Triazine) Membrane for Reverse Osmosis

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Summary

Poly(4-vinylpyridine-co-2,4-diamino-6-vinyl-s-triazine) membranes in which a part of pyridine rings was coordinated with cobalt or copper salt, considerably enhanced salt rejection without appreciable reduction of water permeability. This is attributed to the change in the membrane structure into a polar character. The heat treatment of the uncharged membrane in the salt solution formed the same structure on the surface, but was not effective for improvement of salt rejection, only increasing the membrane strength to a small extent.

Introduction

In our previous papers we have demonstrated that the reverse osmosis performance of the membranes prepared from 4-vinylpyridine (4VP) copolymers with acrylonitrile (OIKAWA et al. 1978) and vinylidene chloride (OIKAWA et al. 1980) was improved by quaternizing with diiodobutane which resulted in charged membranes accompanied with crosslinking. The pyridine ring is also capable of forming not only hydrogen bond with water molecules but also coordinated bond with transition metals (AGNEW et al. 1976). Among nitrogen containing heterocycles other than pyridine ring, diamino-s-triazines or guanamines can form hydrogen bond as well with water and anticipated to give a good water permeability in the membrane application.

In this paper, therefore, we have dealt with the copolymer of 4VP with 2,4-diamino-6-vinyl-s-triazine (DAVT) and investigated the behaviors of the copolymer membranes coordinated with cobalt or copper salt in reverse osmosis. In the case of casting of cellulose acetate membranes the presence of an inorganic

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salt such as magnesium perchlorate and lithium nitrate usually brings about flux enhancement together with rejection lowering to some extent. However, metal coordinated poly(4VP-co-DAVT) membranes revealed an increased rejection compared with that of non-coordinated copolymer membranes.

Experimental

Materials 4VP and dimethyl sulfoxide (DMSO) were distilled under reduced pressure before use. DAVT was prepared from dicyandiamide and 3-dimethylaminopropionitrile (FARBWERKE HOECHST AG. 1969). Commercial pure cobaltic chloride and cupric acetate were dried at 120°C under reduced pressure before use. Poly(4VP-co-DAVT) was prepared by radical copolymerization in DMSO with azobisisobutyronitrile as an initiator (0.25 mole% based on total monomers) at 60°C for 5 hr. The polymer was precipitated into acetone and reprecipitated.
The intrinsic viscosity was measured in DMSO at 25°C.

Preparation of membranes On a glass plate which was wetted with 1% polyacrylamide aqueous solution and dried, 12wt% DMSO solution containing a required amount of a DMSO solution of the salt was cast and dried at 80°C for 1-3 hr. The plate was put in water. The peeled membrane was immersed in water overnight. The thickness of the membranes thus prepared was in the range from 50 to 75μm, mostly about 60μm.

Reverse Osmosis The apparatus and experimental procedures were similar as described in a previous paper (OIKAWA et al. 1978). Nitrogen pressure of 80 kg/cm^2 was applied at 25°C. The molar concentration of Co and Cu salt solution employed for reverse osmosis was the same as that of NaCl (0.06M).
The concentration of the product was determined by electric conductance measurements.

Results and Discussion

The copolymer composition suitable for charging a metal salt was in the range of 55-70 mole% 4VP. The copolymer containing more 4VP have a softer membrane that was difficult to handle. The copolymers comprising more than 45 mole% DAVT,on the other hand, were hard to form a membrane because of their

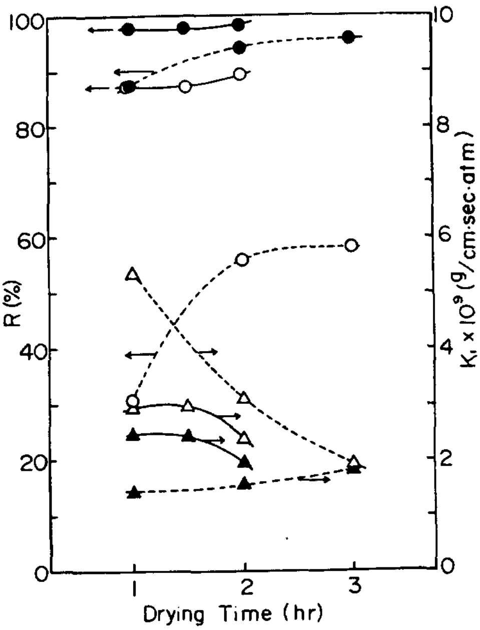


Figure 1

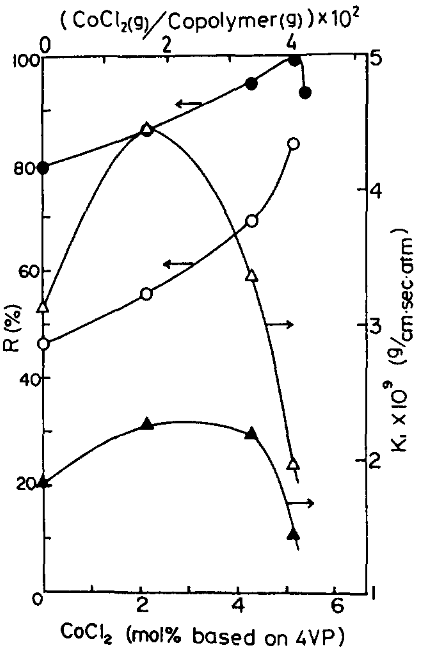


Figure 2

Figure 1 R and K_1 vs. drying time.

------- Uncharged VD-7 (56.8 mole% 4VP, $[\eta] = 0.93$).

——— $Cu(OAc)_2$-charged (2 mole% based on 4VP).

Feed solution: ○△ NaCl, ●▲ $CoCl_2$.

Figure 2 R and K_1 vs. $CoCl_2$ charged.

4VT-11 (69.1 mole% 4VP, $[\eta] = 0.93$).

○△●▲: the same as in Figure 1.

brittle property.

Figure 1 shows the dependence of rejection R and hydraulic water permeability K_1 upon drying time in $Cu(OAc)_2$-charged and uncharged membranes. Three hour was too long to prepare the charged membranes because cracks occurred. Compared with uncharged membranes the Cu coordinated membranes improved R remarkably for the rejection of NaCl and fairly for $CoCl_2$, while K_1 did not vary appreciably at 2 hr drying. The addition of $CoCl_2$ instead of $Cu(OAc)_2$ in casting gave similar results as shown in Figure 2. It also shows the change in R and K_1 with increasing content of $CoCl_2$. R reached a maximum at about 5 mole% charge based on 4VP, beyond which the membrane preparation

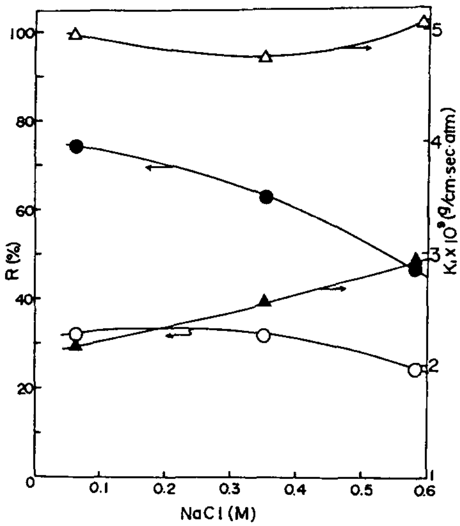


Figure 3

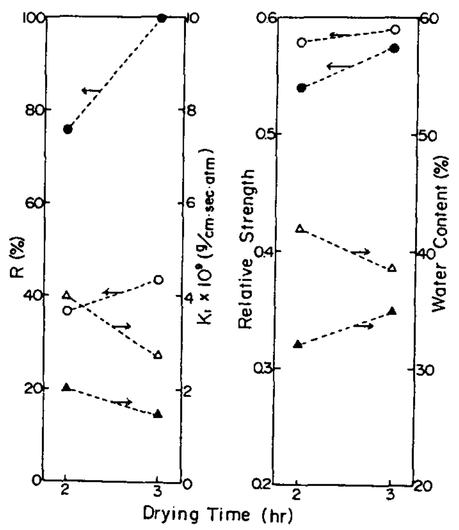


Figure 4

Figure 3 R and K_1 vs. NaCl feed concentration.

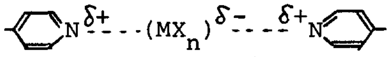
○ △: Uncharged 4VT-15 (66.4 mole% 4VP, [η] = 1.18).

● ▲: $CoCl_2$-charged (4 mole% based on 4VP).

Figure 4 R, K_1, relative strength and water content vs. drying time.

○ △: Uncharged 4VT-10 (56.3 mole% 4VP, [η] = 0.85), treated in 2wt% aq. $CoCl_2$ at 50°C for 1 hr after drying.

● ▲: $CoCl_2$-charged (2.9 mole% based on 4VP).

failed because of cracks. In contrast to R, K_1 showed a tendency to decrease with the content of $CoCl_2$ beyond 2 mole%, probably due to densification by crosslinking of pyridine rings with $CoCl_2$. Figure 2 indicates that, for the copolymer employed, the addition of 4 mole% would be most appropriate since R considerably increased while K_1 remained comparable with that of the uncharged membrane. Of interest was the increase of K_1 up to 2 mole% charge, indicating that the water permeability was enhanced. This may be attributed to the change in the membrane structure; i.e., the coordination of the metal salt with pyridine rings forms a polar structure  $N^{\delta+}\cdots(MX_n)^{\delta-}\cdots{}^{\delta+}N$ and this charged character may have played a principal role to raise rejection in a manner similar as Donnan equilibrium. This was proved, as is shown in Figure 3, by the fact that R of the

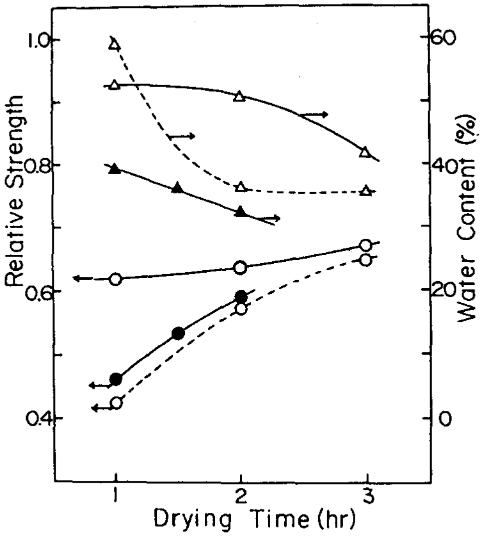


Figure 5 Relative strength and water content vs. drying time.

○ △---- :Uncharged VD-7.
○ △—— :Treated in 2wt% aq. $CuCl_2$ at 50°C for 1 hr after drying.
● ▲—— :$Cu(OAc)_2$-charged (2 mole% based on 4VP).

charged membrane decreased to a greater extent with a higher feed concentration whereas the lowering of R in the uncharged membrane was quite small. The slope of R in the charged membrane was close to that of a quaternized poly(4VP-co-acrylonitrile) membrane (OIKAWA et al. 1978).

A similar polar character can be provided not only by the addition of a metal salt in casting, but also by the heat treatment of an uncharged membrane in the aqueous salt solution, which forms the same coordinated linkages mainly on the surfaces. The performance of the aqueous $CoCl_2$-treated membrane as well as the charged one was shown in Figure 4. The R of the former is strikingly small compared with R of the latter although the K_1 of the former is somewhat higher. The only advantage of this treatment is a slight increase in the relative strength based on cellulose acetate. The similar results were obtained in the membranes treated with a Cu salt, as is shown in Figure 5. On drying for 2 and 3 hr, aqueous $CuCl_2$-treated membranes showed a higher strength in spite of their higher water content. This may be reasoned by the occurrance of the contraction (ca 10% in diameter) in the solution-treated membrane, accompanied with similtaneous densification and local void formation which strengthens the membrane and increases porosity, respectively. K_1 of the treated membranes was about ten times as large as K_1

of the charged membranes, but R of the former was 86% at best in rejection of $CuCl_2$ and lower than that of the latter (97-98%).

Accordingly, it seems necessary for obtaining a high rejection to form the coordinated bond throughout the whole thickness of the membrane by adding metal salt in casting and to increase the density of the polar sites.

The separation behaviors described above resemble to those of ion exchange resins to the effect that the capture of metals by a polymer or their adsorption to a polymer facilitates their separation from the solution. However, the separation with a metal salt-coordinated membrane may have an advantage over the ion exchange method owing to the absence of saturation.

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