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Reverse osmotic properties of the membranes prepared from the polycondensate of 2,5-pyridinedicarboxylic acid chloride and malonyl dihydrazide

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Summary

The membrane performance of the polycondensates derived from 2,5-pyridinedicarboxylic acid chloride and malonyl dihydrazide was studied in reverse osmosis. It depended on drying time, and the kind and amount of a cross-linking agent and an inorganic additive. The membrane strength generally exceeded that of a cellulose acetate membrane. The rejection difference between transition and alkali metal salts was discussed in terms of complexation and the molecular size of the additive. A potential application was suggested for the separation between the two metals through the membrane of a large rejection difference.

Introduction

On the basis of the experimental facts in reverse osmosis that the copolymer membranes which contained functional moieties of coordinating ability like pyridine rings could enhance rejection of inorganic solutes (1) and that the polymer which had a rigid backbone and polar character could give a membrane of excellent performance (2), we have prepared polyhydrazides which contained pyridine rings in the polymer backbone from 2,5-pyridinedicarboxylic acid chloride (PDCC) and dihydrazides of several dibasic acids and studied their dehydration to polyoxadiazoles and the use of the polyhydrazides for reverse osmosis (3). Since further studies on the polyhydrazide membranes revealed that malonyl dihydrazide (MD) brought about a tough membrane, we have dealt in this study particularly with the polycondensates of PDCC and MD and investigated the dependence of their membrane performance on the conditions under which the membranes are formed. The membranes have shown the possibility of separation between transition and alkali metals from their mixture.

Experimental

Materials PDCC was prepared from 2,5-pyridinedicarboxylic acid and thionyl chloride in a similar manner as described previously (3) according to H. Meyer and F. Statten (4). MD was purchased from Wako Junyaku Kogyo Co. and recrystallized from ethanol before use. Commercially available inorganic salts and hexamethylene diisocyanate (HMDI) were used as received.

Polycondensation Interfacial method was employed under similar conditions as reported previously (3) except starting temperature and reaction time (Table 1).

Membrane Preparation On a glass plate was cast with an applicator 8.0~8.8 wt% DMSO solution containing a required amount of an inorganic salt and a cross-linking agent (HMDI) and dried at 80℃ for a given time. The plate was put in water. The peeled membrane was immersed in water overnight. The thickness of the membrane thus prepared was 10~40 μm, mostly 20~30 μm.

Reverse Osmosis Nitrogen pressure of 80 kg/cm^2 was applied at 25℃. Other conditions were the same as before (5). The concentration of sodium chloride (NaCl) and cobaltous chloride ($CoCl_2$) feed was 0.06 M and the product concentration was determined by electric conductivity measurement. Rejection R(%) and hydraulic water permeability K_1 (cm^2/sec・atm) were obtained from the following equations, respectively.

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

$$Jv = K_1\ (\Delta P - \Delta \pi)\ /\Delta x$$

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

Measurements Water content in a wet membrane was estimated in the same way as already described (6). Tensile strength was measured with an instrument Model TOM-5 manufactured by Minebea Co. Ltd. and expressed as a relative value based on the strength of cellulose acetate (CA) membrane prepared by Manjikian's method (7).

Results and Discussion

The results of interfacial polycondensations by dehydrochlorination are summarized in Table 1. The reaction was continued for 120 min as the longest time in the previous report (3), but the present study demonstrated that 30~60 min was sufficient for the reaction and that the difference between room temperature (3) and 10℃ in the starting temperature did not bring any substantial difference in yield and viscosity. Some scatter in the values of yield and viscosity may largely result from a small variation in stirring velocity and probably that in the purity of PDCC.

The resultant polymers were rather poorly soluble in aprotic solvents, but the addition of lithium chloride (LiCl) to the solvent DMSO improved their solubility. The addition of an inorganic salt to a casting dope usually increases the flux and may reduce the membrane strength because of a high porosity. Fig. 1 shows rejection and relative strength with varying drying time for the membranes prepared in the presence of LiCl. The LiCl content of 330 mol% based on the polymer repeating unit corresponds to 35 wt% based on polymer weight, and HMDI of 62 mol% to 29 wt%. R of NaCl gradually increased with time but R of $CoCl_2$ showed a steep increase at 50 min. The strength was higher than that of CA membrane and decreased to a very small extent at 60 min with no

Table 1 Results of interfacial polycondensations[a)]

Code	PDCC in $CHCl_3$,M	MD in H_2O,M	Temp. ℃	Time min.	Yield %	η_{i} [b)]
PMJ3	0.30	0.30	20	30	51.1	0.535
PMJ4	0.30	0.30	20	30	54.4	0.630
PMJ7	0.29	0.30	10	60	48.4	0.508
PMJ8	0.30	0.30	10	60	26.7	0.426
PMJ9	0,28	0.30	10	60	57.7	0.428
PMJ10	0.29	0.30	10	60	70.1	0.451

a) Acid acceptor: NaOH.

b) Inherent viscosity for 0.5 g/dl in a 5% DMSO solution of LiCl at 30℃.

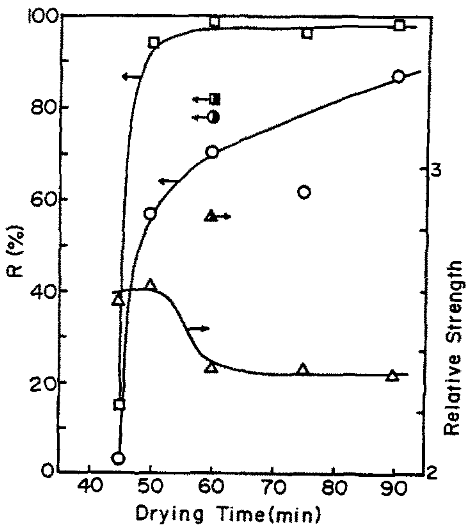
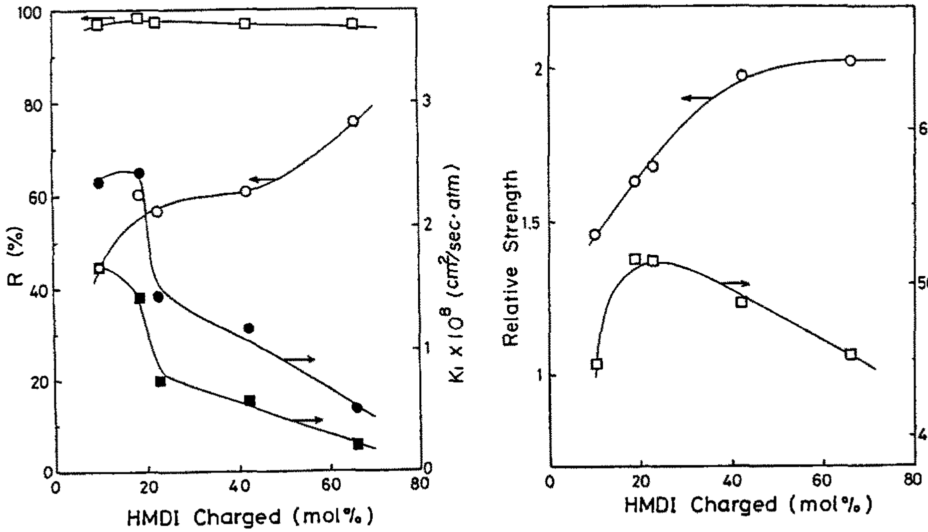


Fig. 1 R and relative strength vs. drying time for PMJ3 membranes charged with 330 mol% LiCl and 62 mol% HMDI based on PMJ repeating unit.
Feed; ○,◑ NaCl, □,◨ $CoCl_2$, ◑,◨,▲ 5.6 mol% $CoCl_2$ charged based on the repeating unit.

further change with prolonged drying. The unexpectedly high strength indicates that the cross-linking by HMDI is so effective as to produce a tough membrane. K_1 decreased monotonously from 1.5×10^{-7} at 45 min to 2.0×10^{-9} at 90 min for NaCl and from 1.0×10^{-7} to 7.4×10^{-10} for $CoCl_2$. They are several times as large as K_1 of the membrane without LiCl. Water content increased with time from 50% to 56%, and the membrane without LiCl had a water content of 36% (relative strength of 2.5) at 60 min while that with LiCl 54%, suggesting that LiCl was still present without leaching out of a membrane and its hydrophilicity contributed to the increase in water content. These values of water content were higher than those of other membranes we ever dealt with. The membrane prepared by drying for 50 min showed a large difference of ca. 40% in R between NaCl and $CoCl_2$ feed. The difference appears to exceed that caused by the difference in metal valence, because 90 min-dried dense membrane showed a small difference in R. The large difference encountered in the membranes prepared at a drying time of 50 min seem to be originated from the capture of $CoCl_2$ by complex formation with membrane material as suggested previously (1,6). Therefore, these membranes are characteristic in their high strength despite of a high porosity, and among them the 50 min-dried membrane in a high flux and a large difference between rejections of transition and alkali metals.

The addition of $CoCl_2$ instead of LiCl to the casting solution gave a

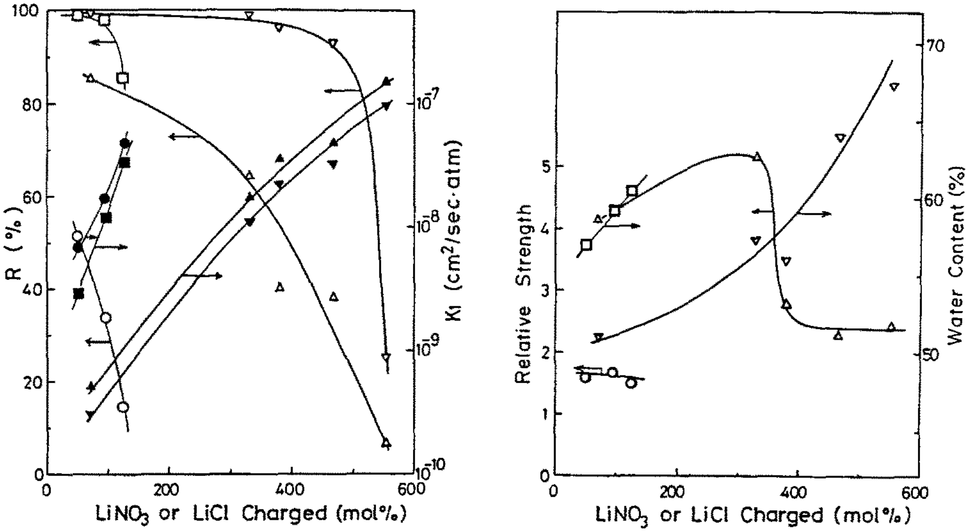


R and K_1 (Fig. 2, left), and relative strength and water content (Fig. 3, right) vs. HMDI charged for PMJ7 membrane containing 330 mol% LiCl and dried for 60 min. Feed in Fig. 2; ○,● NaCl, □,■ $CoCl_2$.

membrane of a small difference in R between the two feeds (Fig. 1) though the strength was higher probably because of cross-linking by coordinating linkages between Co(II) and polymer chains.

The performance of the cross-linked membranes obtained with the addition of an inorganic salt can be altered depending on the kind and amount of the cross-linking agent and inorganic salt. An attempt to use a cross-linking agent other than HMDI, such as diepoxides, divinyl sulfone, and other diisocyanates, could not afford any membrane performance superior to that attained by HMDI, specifically with respect to the strength. Dependence of the performance on the charged amount of HMDI is depicted in Figs. 2 and 3. The increase in HMDI clearly effected the increase in strength owing to the increased cross-linking density and in R of NaCl along with decreasing K_1 and water contents probably because of the increasing hydrophobicity due to methylene groups of HMDI. R of $CoCl_2$ was independent of the amount of HMDI, attributed again to the capture by complexation. Thus, the difference in R at 10 mol% HMDI grew to more than 50%, and this particular membrane may be applicable to the isolation of transition and alkali metal salts from their mixture.

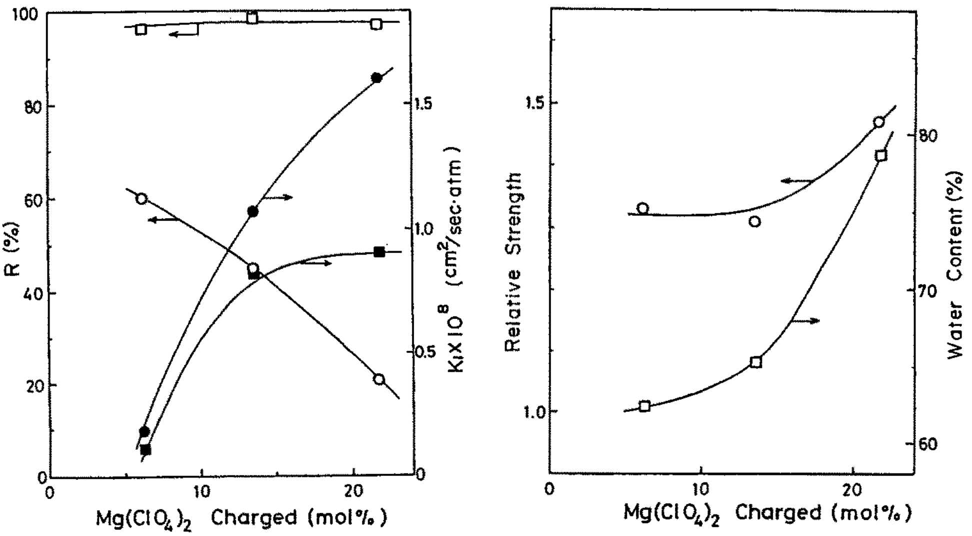
Dependence of the performance on the charged amount of LiCl and lithium nitrate ($LiNO_3$) as another lithium salt is illustrated in Figs. 4 and 5. The addition of a lithium salt more than illustrated gave



R and K_1 (Fig. 4, left), and relative strength and water content (Fig. 5, right) vs. $LiNO_3$ or LiCl charged for PMJ9 membrane containing 18 mol% HMDI and dried for 60 min. Fig. 4; ○,●,□,■: $LiNO_3$, △,▲,▽,▼: LiCl. Feed: ○,●,△,▲: NaCl, □,■,▽,▼: $CoCl_2$.

only weak membranes. The increase in the charge ratio of a lithium salt generally tends to reduce R and enhance K_1. A high rejection of $CoCl_2$ was maintained in a wide addition range of LiCl and the difference in R was maximized at about 400 mol% LiCl. K_1 and the difference in R of the membrane at 380 mol% LiCl were very close to those of the membrane charged with 10 mol% HMDI, but the former membrane was stronger than the latter. At 330 mol% the relative strength was 5, a maximum in the present study. $LiNO_3$ also yielded a membrane of very similar performance at a smaller charge ratio of 100 mol% except for a lower relative strength.

Since magnesium perchlorate ($Mg(ClO_4)_2$) has also been employed as an additive for the flux improvement of CA membrane, the salt was used instead of a lithium salt. The results are shown in Figs. 6 and 7. Addition of a small amount of $Mg(ClO_4)_2$ remarkably changed K_1, water content and R of NaCl. Here again R of $CoCl_2$ remained unaltered, keeping a high value close to 100%. The difference in R in this case reached 76% at 22 mol% charge. Thus, the membrane performance is considerably different depending on the kind and amount of the inorganic additive. The amount of the additive and the performance of the membranes when they showed a maximal difference in R between the two feeds are summarized in Table 2. Apparently, the larger the molecular



R and K_1 (Fig. 6, left), and relative strength and water content (Fig. 7, right) vs. $Mg(ClO_4)_2$ charged for PMJ9 membrane containing 18 mol% HMDI and dried for 60 min. Feed in Fig. 6; ○,● NaCl, □,■ $CoCl_2$.

Table 2 Amount of the additive and performance in the membranes showing a maximal difference in R

Inorganic additive	Amount charged (mol%) a)	Maximal difference in R(%) b)	$K_1 \times 10^9$ (cm²/sec • atm) of feed NaCl	CoCl$_2$	Relative strength
LiCl	380	56.1	35.2	22.2	2.8
LiNO$_3$	100	64.2	17.3	12.0	1.7
Mg(ClO$_4$)$_2$	22	76.2	16.0	9.0	1.5

a) Based on the repeating unit of PMJ.

b) Between NaCl and CoCl$_2$ feed.

size of the additive, the less the amount charged and the greater the difference in R. In other words, an additive of a larger molecular size can yield a greater difference in R with a smaller amount of addition, because the pore size is large enough for NaCl to pass through the membrane while CoCl$_2$ is retained by complexation with the membrane material. Consequently, Mg(ClO$_4$)$_2$-charged membrane is quite unique in its permselectivity and can be used practically for the separation between transition and alkali metals. Moreover, the membrane showed a higher strength than CA membrane in spite of a high water content and was fairly permeable to water, actual fluxes being 40 and 21 l/m² • h for NaCl and CoCl$_2$ feed, respectively. Other inorganic salt of a large size, if soluble in the casting solvent, will bring about similar results.

In conclusion, the polycondensates were capable of forming permselective and tough membranes when cross-linked with HMDI in the presence of a DMSO-soluble inorganic additive of a large molecular size.

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