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Water Permeation and Solute Rejection Behaviors of a Novel Hydrophilic Polyamide Membrane

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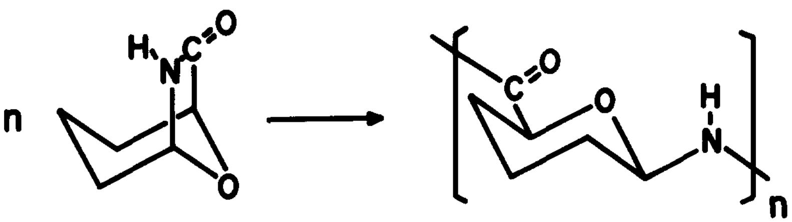
In earlier papers, were described the preparation of a novel hydrophilic polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl) (*1*) by the anionic ring-opening polymerization of a new bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, *2*) and the polymer characterization, including the measurements of water absorption and permselectivity for alkali metal ions (SUMITOMO and HASHIMOTO 1973 and 1977).



(1)

2 *1*

Poly(BOL) membranes were easily prepared under the following different casting conditions:

A. Immersed in water after "casting polymerization" (the room temperature solution polymerization and simultaneous film-casting on a glass or a metal plate; potassium pyrrolidonate, 1 mole% to monomer; molar ratio of DMSO to monomer, 5.6; temperature, 22-24°C; time, 72hr; polymer yield, 41-46%) (membrane No. 1 - 3).

B. Taken out at almost the same polymer concentration as the case of No. 1, in the casting process from 5% DMSO solution of polymer, and immersed in water (membrane No. 4).

C. Drying up at ca. 50°C after casting from DMSO solution of polymer (membrane No. 5 - 6).

The water permeation rate was determined at 25°C under the pressure of $3kg/cm^2$ using a commercial ultrafiltration cell, of which effective membrane area was $13.9cm^2$. As shown in Table 1, poly(BOL) membranes of

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high degree of hydration obtained by immersion in water after casting (casting conditions A and B; No. 1, 2, and 4) permeated a much larger quantity of water than the membrane conventionally cast and dried (condition C; No. 5).

TABLE 1

Water Permeation Through Poly(BOL) Membrane At 25°C Under the Pressure of $3 kg/cm^2$

Membrane No.	Casting condition[a]	Degree of hydration[b]	Thickness,[c] mm	Permeation rate, $l/m^2 \cdot hr$	$K_w \times 10^8$ mole/cm·sec·atm
4	B	0.79	0.38	8.9	17
1	A	0.78	0.50	7.3	19
2	A	0.69	0.45	2.6	6.0
5	C	0.32	0.029	0.25	0.038
Cellulose[d]	-	0.69	0.032	3.9	0.65

[a] A, immersed in water after "casting polymerization". B, immersed in water after casting from DMSO solution of polymer. C, drying up after casting from DMSO solution of polymer.
[b] Volume fraction of water in membrane.
[c] In wet state.
[d] Crosslinked. Data of KAWAGUCHI *et al.* (1975).

The values of hydraulic permeability through the membrane K_w, as well as the water flux J_w, given by the relationship of Eq. (2) much depended upon the casting conditions.

$$J_w = K_w \Delta p / \Delta x \qquad (2)$$

where $\Delta p / \Delta x$ is a pressure gradient (SPIEGLER 1958; KEDEM and KATCHALSKY 1961). The hydraulic permeability through the poly(BOL) membrane tends to increase with increasing the water content. The membrane with the degree of hydration of 0.69 showed about 10 times higher permeability than the crosslinked cellulose of the same degree of hydration.

Great capacities of poly(BOL) membrane for water sorption and permeation may come from the presence of a large number of relatively weak polar sites (MATSUKURA *et al.* 1978), in other words, from the occurrence of polar hydrophilic microdomains surrounded by nonpolar hydrophobic microdomains attributed to the alternating arrangement of an amide linkage and a tetrahydropyran ring along the polymer chains as previously described (SUMITOMO and HASHIMOTO 1977).

The solute rejection test for the poly(BOL) membrane was also coducted using the ultrafiltration cell at 25°C under the pressure of $3kg/cm^2$. The concentrations of aqueous solutions of sodium chloride and urea were determined by means of conductometry and differential refractometry, respectively. For all of the other solute, UV spectrophotometry was adopted. The results are listed in Table 2.

TABLE 2

Solute Rejection from Its Aqueous Solution by Poly(BOL) Membrane[a]

Solute	Mol. wt.	Rejection, %	
		Thickness of membrane, mm	
		0.58[b]	0.035[c]
Sodium chloride	58.5	22	-
Urea	60	-	0
Creatinine	113	3	28
Uric acid	168	14	-
D-(+)-Glucose	180	8	-
Vitamin B_{12}	1,355	78	42
Myoglobin	17,800	88	-
Albumin[d]	67,000	94	94
γ-Globulin[d]	175,000	98	-

[a] Operating pressure, $3kg/cm^2$; temperature, 25°C; concentration of feed solution, 0.005 - 0.5%.
[b] Membrane No. 3; casting condition A ("casting polymerization"); degree of hydration, 0.73; permeation rate, 1.9 $l/m^2 \cdot hr$.
[c] Membrane No. 6; casting condition C (drying up after casting); degree of hydration, 0.27; permeation rate, 0.11 $l/m^2 \cdot hr$.
[d] Bovine serum.

The relatively thick membrane prepared by "casting polymerization" rejected about 80% of vitamin B_{12} (MW 1,355) from its aqueous solution. Globular proteins of high molecular weights were almost completely rejected by the membrane, while most of such low molecular weight solutes as creatinine and uric acid permeated. Some extent of rejection was peculiarly observed for sodium chloride. Throughout these ultrafiltration tests the hydraulic permeation rate was constant and almost the same as of pure water.

The thin membrane dried up after conventional casting rejected only 42% of vitamine B_{12}, although its rejection ability for creatinine was higher than that obtained by the "casting polymerization".

SUMMARY

The poly(BOL) membrane prepared by "casting polymerization" exhibited an excellent fractional solute-rejection behavior in the aqueous solution, having a comparatively sharp boundary region at the molecular weight range of about 200 to 1400, together with an extremely high water permeability. These conspicuous behaviors, as well as a great capacity for water absorption, may result from some delicate arrangement of polar hydrophilic and nonpolar hydrophobic microdomains probably formed along and between the polymer chains.

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