Preparation, Characterization and Gas Permeability of Asymmetric Porous Membranes of Poly(carbobenzoxyl-L-Lysin)

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비대칭 다공성 폴리(카르보벤족시-L-리신)막의 제조, 평가 및 기체투과

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요 약 : 질소가스에 대한 헬륨가스의 선택도가 매우 높은 poly(carbobenzoxy-L-Lysin)(PCLL)로 제조된 균일막의 투과도를 증가시키기 위해서 디옥산과 DMF의 20% 용액을 이용하여 캐스팅법으로 비대칭 다공성막을 제조하였다. 이 막에 대해서 표면에서의 공극의 수와 공극크기의 분포를 측정하였으며, 표면층의 두께는 주사전자현미경과 투과전자현미경을 이용하여 측정하였다. 평균공극크기와 평균공극밀도는 DMF용액보다 디옥산용액으로 제조한 경우 더 낮은 값을 나타내었으며, 이는 비대칭 다공성막에 있어서 공극의 형성메카니즘으로 설명할 수 있다. 투과계수는 표면층을 통한 점성흐름으로 어느 정도 설명될 수 있으나, 선택도는 점성흐름의 이론과 대치되었다.

Abstract: In order to improve the permeability of the homogenous membrane of poly(carbobenzoxy-L-lysin)(PCLL), which has very high selectivity of helium gas to nitrogen gas, asymmetric porous membranes of PCLL were prepared by casting from 20% solutions in dioxane and dimethylformamide(DMF), respectively. The membranes were characterized by measuring the number of the pores, the pore size distribution of the surface(the skin layer) and the thickness of the skin layer by scanning electron microscope and transmission electron microscope. The mean pore size and the pore density were lower for the membrane cast from dioxane than that from DMF, which was explained by the mechanism of the formation of the pores in the asymmetric porous membrane. The permeability coefficient observed could be roughly explained by the viscous flow through the skin layer. However, the selectivity observed was against the theory of the viscous flow.

1. Introduction

In membrane processes using polymeric membranes, many efforts had been concentrated on improving both selectivity and permeability, because these two parameters usually show an inverse relationship in the case of homogenous membranes[1]. One of these efforts is a facilitated transport using the asymmetric membrane with quite thin skin layer, which actually controls the permeability[2-

8]. Polymeric porous membranes have been used for ultrafiltration in which membranes filter molecules depending on their sizes[3, 5]. We have systematically[9-13] studied the gas permeability through the porous membranes and also the mechanism of the formation of the asymmetric membrane [14].

Very high selectivity has been reported on homogeneous membranes of poly(amino acid)s[15, 16]. This is considered to be due to the molecular sieve effect depending on the conformation and texture of poly(amino acid)s in the membrane[16]. However, the permeability of the membrane is very low. In this paper, therefore, we attempted to make asymmetric membranes of poly(carbobenzoxy-L-lysin) (PCLL) to improve the permeability of the homogeneous membrane since the permeability of the membrane is inversely related with the membrane thickness. In order to characterize the porous nature of the membrane, we used inert gases, helium(He) and nitrogen(N_2), as the penetrant to deliberately avoid any special interactions with the membrane. Since poly(amino acid) membrane is biocompatible, however, this study will be useful for potential artificial lung[17].

2. Experimental

2. 1. Materials

N‐carbobenzoxy‐L‐Lysin(cbz‐L‐Lys) N‐carboxyanhydride(NCA) was prepared from L‐lysine monohydrochloride(L‐Lys HCl) in the usual manner as reported previously[18]. NCA was polymerized in its solution of 0.5mol/l in dioxane at 30℃ for 24hrs., using triethyl amine as an initiator to obtain poly(N^{ε}-carbobenzoxy-L-lysin)(PCLL). The molar ratio of the NCA to the initiator, [A]/[I], was 50.

Gases used as the penetrant were He and N_2 supplied from Nihon Sanso Co. and of 99.9% purity.

2. 2. Methods of preparation of membrane

Thin films of PCLL were cast on a glass plate or

mercury with 0.5mm thick from the 20% solutions in dioxane and dimethyl formamide(DMF), respectively, at 20℃ and 50% relative humidity. Immediately after the casting, films were immersed in water at 18℃ for 6hrs., washed with water, dried in air and later under vacuum for 24hrs. The thickness of the membrane cast from the solution in DMF (Membrane Ⅰ) was 280 μm and that from the solution in dioxane(Membrane Ⅱ) was 200 μm, respectively.

2. 3. Characterization of the membrane

Pores of the PCLL membranes prepared were directly observed by a scanning electron microscope (SEM, model HU-11c of Hitachi Co.) and a transmission electron microscope(TEM, model JSM-U3 of JEOL, Japan). Pore size distribution, mean pore size and pore density were calculated from the photographs.

2. 4. Measurement of gas permeability

The instrument used is already reported in our previous studies[9−11]. The pressure in the higher pressure side, p_1, was adjusted to 25, 40 and 55cmHg, respectively. The pressure in the lower pressure side, p_2, was measured as a function of time by a mercury manometer. The permeability coefficient, $P(p_1, p_2)$ in the unit of cm³(STP)/cm · sec · cmHg, was calculated by[9-11] :

$$P(p_1, p_2) = \frac{T_0}{T} \frac{\ell V}{p_0 A(p_1 - p_2)} \qquad (1)$$

where, T_0, the standard temperature(273.2K), T, the measuring temperature, p_0, the standard pressure(76 cmHg), ℓ, the membrane thickness(cm), A, the membrane area(cm²), V, the volume of the lower pressure side(cm³), and dp_2/dt is the slope of the pressure in the lower pressure side vs. time (cmHg/sec). The thickness of the skin layer, ℓ, was about 2μm for both membranes from the SEM micrographs of the cross sections of the membranes. The difference in the thickness of the skin layer between Membranes Ⅰ and Ⅱ could not be distin-

Table 1. Characterization of Pore of PCLL Membranes

Characteristic value	Membrane I	Membrane II
N(number/cm²)	4.34×10^6	1.96×10^6
$\bar{\gamma}(\mu m)$	0.241	0.190

guished within the experimental error of ±3%. Thus, the apparent permeability usually used for the asymmetric membranes must be nearly 100 times larger than the observed value.

3. Results and discussion

3. 1. Characterization of the membranes

From the SEM micrographs of the cross-section of the membranes(not shown here), we confirmed that these porous membranes have asymmetric structure in which the surface is a skin layer of about 2μm thickness, as mentioned above. As many investigators pointed out, the skin layer controls the permeability of the membrane and porous layer underneath only acts as the supporter of the skin layer.

In this case, however, the skin layer is not the active homogeneous layer, but also a porous layer. TEM micrograph of the surface(the front side) of the membrane showed pores with 0.2~0.4μm of radii. On the other hand, SEM micrographs of the back side, which had been contacted with the glass plate or mercury on casting, showed much bigger pores, the radii of which were 2~3μm.

From many TEM micrographs of the surfaces (the front side) of the membranes, the density of the pores, N, the number of pores in unit area, and the mean radius, $\bar{\gamma}$, were determined. Table 1 shows N and $\bar{\gamma}$ for the membranes I and II. Although the differences are not much, both the pore density and the mean pore radius are higher for the membrane I than for the membrane II.

Now, the mechanism of the formation of pores in the asymmetric membrane has been nearly established, in terms of microphase separation[2-5]. The above result may be explained as follows. DMF
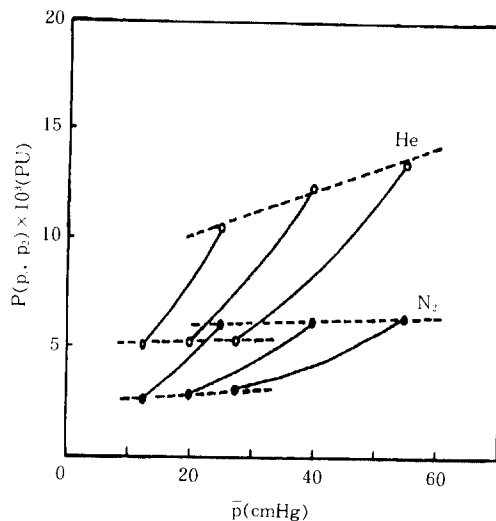

Fig. 1. Mean pressure $\bar{p}$ dependence of gas permeability coefficient $P(p_1, p_2)$ of the PCLL membrane for He and N_2.

being better solvent of PCLL than dioxane, the supersaturation in the interface between the solution and water should be higher for the PCLL-DMF-water system than for the PCLL-dioxane-water system. On the onset of phase separation in the interface, therefore, larger number of smaller droplets of the polymer-lean phase should be formed(in the polymer-rich phase) in the case of DMF, as compared with the case of dioxane. In the process of the coarsening in the spinodal decomposition followed, the droplets may aggregate into bigger particles, resulting finally the pores bigger for DMF than for dioxane, keeping the relative density of pores higher for DMF than for dioxane.

3. 2. Gas permeability

In Fig. 1, the permeability coefficient, $P(p_1, p_2)$, of the PCLL membrane cast from the solution in DMF is plotted against the mean pressure, $\bar{p}$, i. e., $(p_1 + p_2)/2$. The full curves are experimental data, obtained on fixing p_1, as 25, 40, 55cmHg, respectively. The upper broken curve indicates the case, where $\bar{p} = p_1$, namely, $p_2 = p_1/2$, and the lower does the case, where $\bar{p} = p_1/2$, namely $p_2 = 0$. It is seen that the permeability coefficient is dependent
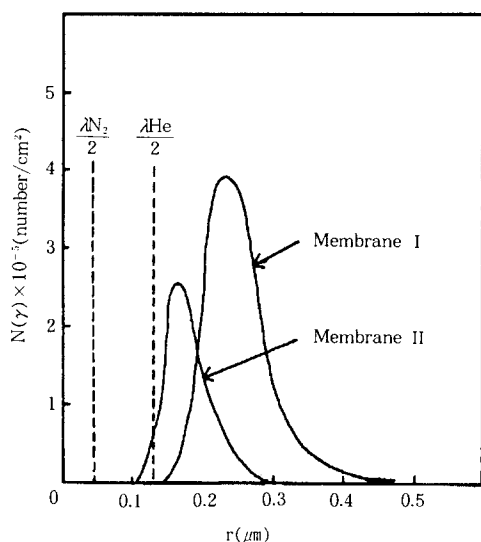
Fig. 2. Pore size distribution functions, $N(r)$, of the PCLL membranes, compared with the mean free path of N_2, and that of He.

on the mean pressure and is larger for He than N_2.

It is known[2] that when the mean free path, λ, of the gas is larger than the diameter(i. e., 2γ) of the pore of the membrane, the flow of the gas through the membrane should be the free molecular flow, which is independent of the pressure difference, p_1-p_2. Therefore, the above results suggest that the viscous flow prevails in this case. The permeability coefficient of the viscous flow is expressed by[2]:

$$P(p_1, p_2) = N\pi\gamma^4 \cdot \frac{\bar{p}}{p_0} \cdot \frac{1.013 \times 10^6}{76} \cdot \frac{T_0}{T} \qquad (2)$$

where, N is the number of pores in the unit area (cm²) of the membrane and is the gas viscosity. This shows that the permeability should be dependent on the mean pressure, $\bar{p}$, which is consistent with the above data.

Fig. 2 shows the pore size distributions of the two PCLL membranes, together with the free molecular paths of He and N_2. It is evident that the pore sizes of both membranes are larger than the half of the mean free path of He and N_2. Table 2 shows the permeability coefficient, $P(0, 0)$, which was ob-

Table 2. Permeability Coefficients of PCLL Membranes

Membrane	Permeability coefficient $P(0,0)$ cm³(STP)/cm · sec · cmHg		P_{He}/P_{N2}
	P_{He}	P_{N2}	
I [1]	5.0×10^{-3}	2.2×10^{-3}	2.3
	(1.7×10^{-3})	(1.9×10^{-3})	
II [2]	3.4×10^{-4}	0.42×10^{-4}	8.1
	(3.3×10^{-4})	(3.6×10^{-4})	

[1]PCLL/DMF, [2]PCLL/Dioxane

Table 3. Permeability Coefficients of Membranes

	Permeability coefficient $P(0,0)$ cm³(STP)/cm · sec · cmHg		P_{He}/P_{N2}
	P_{He}	P_{N2}	
Silicone rubber	2.3×10^{-8}	1.5×10^{-6}	1.5
Polycarbonate	6.7×10^{-9}	0.46×10^{-9}	15
Teflon FEP	6.2×10^{-9}	0.25×10^{-9}	25
Natural rubber	3.6×10^{-9}	1.05×10^{-9}	3.4
Membrane I	5.0×10^{-3}	2.2×10^{-3}	2.3
Membrane II	3.4×10^{-4}	0.42×10^{-4}	8.1
PCLL	5.0×10^{-11}	1.5×10^{-13}	330

tained by extraporation from such curves as in Fig. 1, for two membranes, and the selectivity, $P(0, 0)_{He}$ $/P(0, 0)_{N2}$. The values calculated by Eq. (2) are also shown in the parentheses in the table. The experimental values are nearly in accord with the calculated, except the value of $P(0, 0)_{N2}$ for the Membrane II. Thus, we repeated the experiment for this case, but the result was reproducible. However, in spite of the fact that the theory predicts the higher permeability coefficient of N_2, due to the lower viscosity of N_2 than those of He(see Eq. (2)), the permeability coefficient observed is apparently higher for He than N_2 for both membranes. For the free molecular flow, the permeability should be higher for He than N_2 due to the lower molecular weight. Even when the parallel model of the composite structure[19] of the viscous and free molecular flows was assumed, the area of the pore size distribution below $\lambda_{He}/2$ is too small to explain the result.

Table 3 shows the comparison of the present data

with those obtained for other homogeneous polymer membranes[15]. It is obvious that our porous membranes have much higher permeability than other homogeneous membranes. Among these homogeneous membranes, the PCLL membrane has quite high selectivity of He against N_2, as mentioned in the introduction section. If we simply assumed the additivity of the selectivities of the porous and homogeneous parts of the membrane, the contribution of the porous part can be calculated to be 99.7% for the Membrane I and 97.5% for the Membrane II, which looks like reasonable. However, the permeability for the two gases is too high to explain the contribution of the homogeneous part by the parallel model mentioned above[19]. Only possible explanation left may be as follows. In the course of the membrane formation in this case, a certain amount of pore capillaries may be barried underneath the surface. If the depth of the top part of capillary from the surface was sufficiently short(for instance, in several tens of Angstrons), the permeation through this homogeneous layer of the polymer may well contribute to the over-all permeation (though to a small amount), thus giving rise the selectivity of He gas to N_2 gas as the whole, due to the very high selectivity of the homogeneous PCLL membrane(Table 3). The higher experimental values of the permeability coefficient than the theoretical values, except P_{N2} for Membrane II, may be due to the rough estimate of the thickness of the skin layer.

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