The Effect of a Photo-induced pH Change on the Hydrodynamic Permeability through Porous Membrane with Adsorbed Poly(L-glutamic acid)

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Reversible pH changes of aqueous solution, although the degree of the pH change was small, were induced by a photo-oxidation of leuco malachite green in CCl_4 phase in the aqueous solution. This photo-reaction was applied to control pH of the bathing solution when the volume flux through porous membrane with adsorbed poly(L-glutamic acid)(PGA) was measured as a function of pH gradient across the membrane. It was confirmed that the conformational change of the adsorbed PGA on the pore walls was induced by the photo-induced pH change of the bathing solution. The rate of the conformational change of the adsorbed PGA was remarkably faster than that of PGA in the solid state. As a result, a oscillatory volume flux through the porous membrane was observed by on-off switching of the uv lamp *via* a photo-oxidation of the leuco dye in the bathing solution.

Stimuli-responsive membranes have been of great interest recently, since they have some characteristic functions such as regulation of drug release^{1,2)} and energy conversion media^{3,4)}. In previous studies, we have shown that transport properties of poly(α -amino acid) membranes are to be controlled by pH-induced conformational change of PGA^{5,6)}, redox-controlled conformational changes of poly(L-cystein)⁷⁾ and trans-cis isomerization in side chain azobenzene groups of azobenzene-modified PGA^{8,9)}. We have also shown that the volume flux through a

porous membrane with adsorbed PGA was strongly dependent on the pH gradient across the membrane¹⁰⁾. In this communication, we report on a rapid reversible change in the volume flux through the membrane resulting from the conformational changes of the adsorbed PGA on the pore walls caused by a photo-induced pH change of the bathing solution in a half cell containing a photochromic leuco dye.

PGA was prepared by the saponification reaction of poly(γ -methyl L-glutamate) (kindly provided by Ajinomoto Co. Ltd.) with aqueous solution of sodium hydroxide as described previously⁵⁾. PGA adsorbed filter was prepared by placing the filter(Millipore filter; pore size of $0.1\mu\text{m}$ and Nuclepore filter; pore size of $0.05\mu\text{m}$) in a vessel containing aqueous solution of PGA ($0.1\text{g}/100\text{ml}$) at pH 4.0 without added salt. The volume flux through the porous membrane was measured by a pyrex glass permeation cell as was shown in Figure 1. The volume flux, J_v , was determined by observing the level of meniscus of water in the capillary tube of 0.124cm radius, which was attached to the permeant side cell, using a cathetometer. The filtration coefficient, L_p , was determined using $L_p = J_v/\Delta p$, where Δp is the pressure difference between the membrane. pH jump of the solution in the high pressure side of the cell was achieved by applying uv irradiation to the half cell containing leuco malachite green(0.03g)/ CCl_4 (10ml) as

Fig.1 Apparatus used for the permeation experiment.

C; capillary, M; porous membrane, S; magnetic stirrer.

The high pressure side of the cell (206 ml) contains leuco malachite green (0.03 g)/CCl₄ (10ml).

shown in Figure 1. Repeated reversible pH change was achieved by switching the uv lamp on and off. Irradiation was carried out with a 100W high-pressure mercury lamp (Rico-Kagaku Sangyo Co. Ltd., UVL 100p).

Figure 2 shows the relation between the volume flux and the pressure difference across the membrane when a pH gradient existed between the two external solutions separated by the membrane (pH 9.0 | membrane | pH 4.0). An asymmetric curve in the J_v - Δp relation was obtained. The original Millipore filter without PGA showed that J_v monotonously increases with Δp . This result indicates that the conformational gradient of PGA through the membrane pores was made under the pH asymmetry across the membrane¹⁰. In the next step of controlling the conformation of the adsorbed PGA, a pH gradient across the membrane was induced by photoirradiation. Halocarbon-sensitized photo-induced oxidation of triphenylmethane leuco derivatives is a well-known reaction. MacLachlan¹¹ has shown a number of stepwise photo-oxidation reactions of leuco ethyl violet in the presence of CCl₄, yielding HCl, H⁺ and the corresponding dye. This suggests that triphenylmethane leuco derivatives may be useful for controlling the pH of aqueous solution upon uv irradiation. Figure 3(c) shows the photo-induced pH decrease of aqueous solution in the high pressure side of the

Fig.2 The relation between the volume flux, J_v , under a pH gradient (pH 9.0 | membrane | pH 4.0) and the pressure difference across the membrane, Δp , at 25°C. The values of J_v from pH 4.0 side to pH 9.0 side are positive.

cell containing leuco malachite green dissolved in CCl₄ phase (Figure 1). The pH was decreased from 6.2 to 5.7 by irradiation within a few second. After removal of the light, the pH returned to the initial value in a few minutes. The longer uv irradiation was applied, the larger the pH decrease was observed, however, the pH did not return to the initial value in the dark owing to the dissolution of the leuco dye to the aqueous phase from CCl₄. Therefore, the reversible pH change can be achieved by an instantaneous uv irradiation. The dependence of the filtration coefficient, L_p , on the photo-induced pH change in the high pressure side of the cell was observed at 25°C, using Millipore and Nuclepore filters, respectively. The results are shown in Figure 3(a) and (b). Rapid changes in L_p were observed for both membrane systems resulting from the photo-induced pH asymmetry across the membrane. In addition, it is clear that the L_p changes in Figure 3(a) and (b) were entirely consistent with the photo-induced pH changes in the high pressure side of the cell (Figure 3(c)). It was already shown¹⁰ that L_p of the porous membrane with adsorbed PGA was

Fig.3 (a) Photo-induced L_p changes of Millipore filter with adsorbed PGA at 25°C.
 (b) Photo-induced L_p changes of Nuclepore filter with adsorbed PGA at 25°C.
 (c) Photo-induced pH changes of aqueous solution in the high pressure side of the cell containing leuco malachite green/ CCl_4 at 25°C.

strongly dependent on the conformation of PGA on the pore walls. Figure 3 indicates, therefore, the rate of conformational changes of PGA on the pore walls was determined by the rate of the photo-oxidation reaction of the leuco malachite green, i. e., PGA itself changes own conformation within a second. On the other hand, the rate of the conformational change of PGA in the solid membrane was shown to be ca. 10^5 second¹²⁾. The slower the conformational change of PGA in the solid state can be attributed in part to the slower H^+ (or OH^-) diffusion rate in the solid membrane phase compared with that in the liquid phase of the present membrane pores. The bars inserted in Figure 3(a) and (b) indicate the degree of change in L_p for both membrane systems (Millipore and Nuclepore filters) owing to the pH change from 6.2 to 5.7 when the pH of the solution of both sides of the membrane was identical. The photo-

induced changes in L_p are smaller than the corresponding changes in L_p under iso-pH changes across the membrane for both systems. Therefore, the photo-induced pH asymmetry across the membrane maintained a conformational gradient of PGA through the pores of the membrane. The difference between the photo-induced L_p change and that under iso-pH condition for Nuclepore filter, however, is smaller than that for Millipore filter, indicating that the conformational gradient of the adsorbed PGA in Millipore is remarkable. This result can be ascribed to the difference in membrane thickness, i. e., the thickness of Nuclepore, ca. $5\mu\text{m}$, is thinner than that of Millipore, ca. $92\mu\text{m}$. It may say, therefore, that the rate of the conformational change of the adsorbed PGA is mainly determined by the diffusion rate of H^+ ions, which were produced by the photo-oxidation reaction of leuco malachite green, through the pores.

These results indicate that the membrane with oscillate pore size can be made resulting from a periodical conformational change of the adsorbed PGA within the pores via the photo-induced pH asymmetry across the membrane.

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