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Generation of Osmotic Pressures through a Molecular Recognition Ion Gating Membrane

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The molecular recognition ion gating membrane, which is a bio-inspired membrane comprising the copolymer of N-isopropylacrylamide and benzo[18]-crown-6-acrylamide grafted onto the surface of a porous polyethylene film, responded to both a change in temperature and a specific ion signal. The gating membrane generated similar osmotic pressures to a dialysis membrane in the closed-pore state but not in the open-pore state. An optimized membrane structure was required for controlling this phenomenon. Generation of the osmotic pressure was closely related to the ion distribution through the membrane thickness.

Key words: crown ether, N-isopropylacrylamide, membrane, molecular recognition, osmotic pressure

1. INTRODUCTION

There is a great difference between the performance and functionality of biomembranes and artificial membranes. Some bio-inspired membranes have been found to mimic biomembranes, and then go beyond them [1-4]. We have studied a molecular recognition ion gating membrane that responds to a specific ion signal that controls its functions, such as hydrostatic flow [5] and diffusivity [6]. The copolymer of N-isopropylacrylamide (NIPAM) and benzo[18]crown-6-acrylamide (BCAm) was grafted onto the porous surface of a porous film. NIPAM is a thermosensitive polymer, and acts as an actuator by its volume phase transition. BCAm has a crown ether receptor that functions as an ion sensor [7]. Thus, the membrane captures only the specific ion whose size fits the cavity of the crown ether receptor, and then swells the grafted copolymer.

Recently we found that this membrane can control osmotic pressure [8,9]. Under a concentration gradient of ions or polymers, such as dextran, the membrane generated an osmotic pressure when its pores were closed, while the osmotic pressure disappeared when its pores were open (see Fig. 1). Furthermore, under specific conditions, the pressure triggered a nonlinear oscillation [10]. In this paper, we focus on the relationship between the osmotic pressure response and selected membrane properties, such as (i) the amount of grafting of the copolymer, and (ii) the ion concentration distribution inside the membrane.

2. EXPERIMENTAL

2.1. Membrane preparation:

The membrane was prepared by the peroxide plasma graft copolymerization method, as described in earlier publications [5,6,8-10]. Grafting ratios, defined as the volume of the grafted copolymer divided by the pore volume of the substrate, were 6.5% and 14.6%. High-density porous polyethylene (HDPE) film (Asahi Chemicals; pore size 0.2 μm, thickness 100 μm) was used as a substrate. Plasma treatment power and time were 30 W and 1 min, respectively. A grafting ratio of 14.6% was generally used for the membrane in the following osmotic pressure measurements, unless otherwise stated.

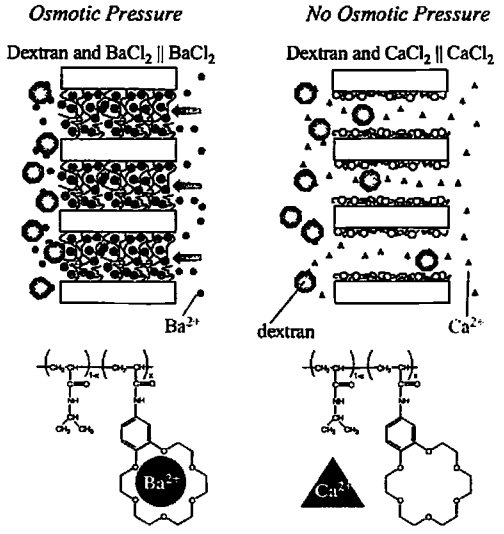

Fig.1 Concept of osmotic pressure control through a molecular recognition ion gating membrane under a dextran concentration gradient

2.2 Osmotic pressure measurements:

Osmotic pressure was measured using an osmometer cell [11] at various temperatures between 20 and 43.5°C. The osmometer had a solution chamber and a solvent chamber, and the membrane was placed between these two chambers. The solution chamber was filled with an ion solution, or an aqueous mixture of an ion solution and a dextran solution, and then closed by a valve to prevent the inflow of solvent. The increase in pressure inside the solution chamber was detected by a pressure sensor (KEYENCE, AP-12A), and recorded using a personal computer at intervals of 1 min. The solvent chamber was filled with pure water or an ion solution. Dextran T500, T70, and 4 (Mw = 470 000, 74 000, and 4000) were used as the solute to generate the osmotic pressure, and $BaCl_2$ and $CaCl_2$ were used as signal ions.

3. RESULTS and DISCUSSION

3.1 Thermosensitivity of the osmotic pressure generation of the gating membrane:

Because poly-NIPAM responds to a temperature change, the gating membrane can respond to a temperature change and change its pore size without an ion signal. Osmotic pressures through the gating membrane, between an aqueous solution of 0.2 g/ml dextran T500 and pure water, were measured at various temperatures (see Fig. 2). Solutions contained $CaCl_2$ only at 42°C. The membrane generated an osmotic pressure at 20°C in pure water, and the value corresponded to the osmotic pressure through a dialysis membrane (MWCO = 14 000). This means that the gating membrane behaves as a semipermeable membrane when the grafted copolymer swells and its pores are filled with the grafted copolymers. The gating membrane did not generate an osmotic pressure at 42°C because at this temperature the pores are completely open.

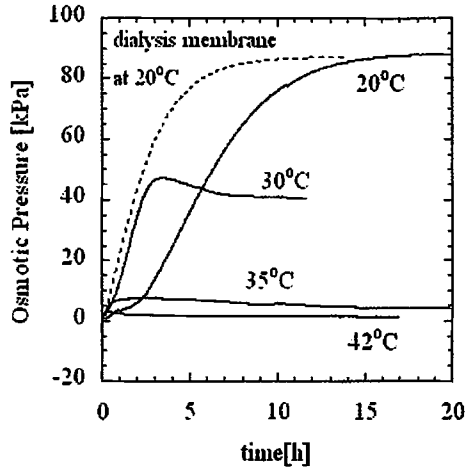

Fig2. Osmotic pressures in pure water at various temperatures

3.2 Dependency of osmotic pressures on molecular weights of dextrans and signal ions:

Based on the results shown in Fig. 2, changes in pore size control the osmotic pressure. Thus, a change in pore size induced by ion signals can control osmotic pressures, as shown in Fig. 1. Furthermore, an osmotic pressure is generated when a solute is rejected by the membrane. Especially in the case of a porous membrane, the rejection is determined by the ratio of the pore size to the solute size. Thus, the molecular weight of the dextrans can have an effect on the osmotic pressure.

Based on the above, we measured the osmotic pressures in $BaCl_2$ and in $CaCl_2$ solutions, using dextran T500, dextran T70, or dextran 4 (0.2 g/ml) to generate a concentration gradient (see Fig. 3). In the case of Ba^{2+}, osmotic pressures were generated in dextrans of all three molecular weights, while in the case of Ca^{2+}, osmotic pressures were almost zero in the dextrans. Crown ether receptors in the gating membrane caught the Ba^{2+} ions and the pores closed. Likewise, osmotic pressures were generated in the same way at low temperatures. However, the time course of the generation of osmotic pressures differed for the dextran solutions of different molecular weights. Dextran with the highest molecular weight, dextran T500, resulted in the highest osmotic pressure. Dextran with the lowest molecular weight, dextran 4, resulted in a quick increase in the osmotic pressure but there was also a quick decrease, and the final pressure was the lowest. Furthermore, in the case of Ba^{2+}, the maximum pressures were lower than in the case of pure water at 20°C (see Fig. 2). In other words, in the case of Ba^{2+}, the pores did not close as well as in the case of water. On the other hand, dextran 4 (Mw 4000) generated an osmotic pressure; thus, the pore size may be below about 1.6 nm.

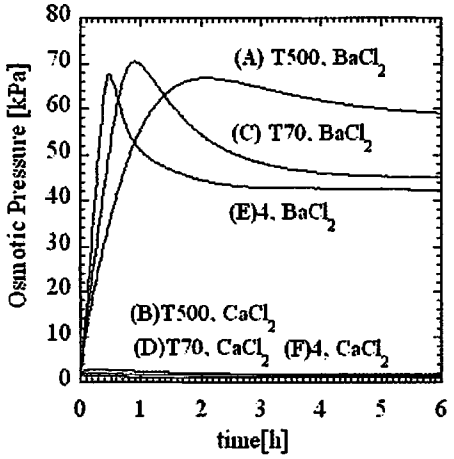

Fig 3. Dependency of osmotic pressure on dextran molecular weight and ion species. Dextran and ion concentration were 0.2g/ml and 0.1M, respectively.

(A)(B) : dextranT500(Mw=470000) at 42°C,

(C)(D) : dextranT70(Mw=74000) at 43.5°C,

(E)(F) dextran4(Mw=4000)at 43.5°C.

(A)(C)(E) : $BaCl_2$ and (B)(D)(F) :$CaCl_2$.

3.3 Effect of grafting ratio on osmotic pressures:

The membrane structure, especially the grafting ratio, is a very important factor in the generation of the osmotic pressure. The gating membrane with a 14.6% grafting ratio generated the osmotic pressures shown in Fig. 3, whereas the gating membrane with the 6.5% grafting ratio did not generate an osmotic pressure, even in the presence of Ba^{2+} (see Fig. 4), though both the membranes changed pressure-driven flow in response to ion signals (data not shown).

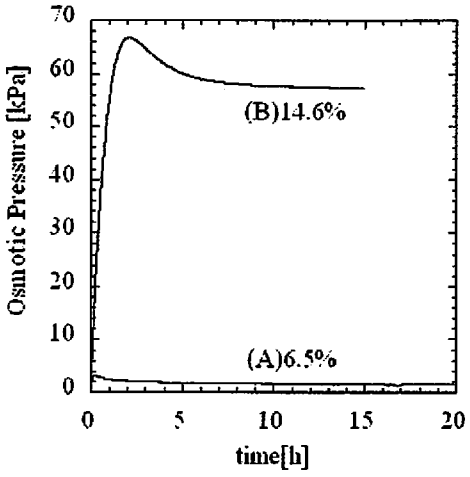

Fig 4. The effect of grafting ratio on osmotic pressure generation at 43.5°C. Dextran and $BaCl_2$ concentration was 0.2mg/ml and 0.1M, respectively. Data (B) has already shown in data (A) in Fig.3.

3.4 Effect of the initial concentration of Ba^{2+} in the gating membrane on osmotic pressures:

The initial concentration of Ba^{2+} in the gating membrane had an effect on the osmotic pressure generation. The membrane was immersed either in pure water or in a 0.1 M $BaCl_2$ aqueous solution, and then the osmotic pressures were measured (see Fig. 5). The osmotic pressure increased quickly initially when there were no ions, but gradually increased in the presence of $BaCl_2$.

Finally, the osmotic pressure reached the same value in both cases, because the ions diffused into the membrane and the ion concentration gradient between the feed solution and the gating membrane disappeared after several hours.

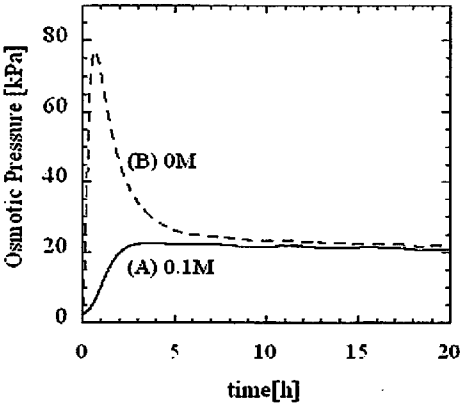

Fig 5. Dependency of the time course of osmotic pressures on the initial ion concentration of Ba^{2+} in the membrane at 38 °C. Dextran T500 concentration was 0.1g/ml and $BaCl_2$ concentration was 0.1 M. Initial $BaCl_2$ concentration was (A)0.1 M or (B)0 M.

3.5 Counter diffusion of Ba^{2+} and Ca^{2+} and osmotic pressure generation:

Signal ion distributions through the gating membrane determine swelling phenomena of the grafted copolymer, and thus pore size changes within the membrane. This distribution results in a change in the osmotic pressure generation.

Respective solutions of 0.1 M $BaCl_2$ and $CaCl_2$ were placed in a dextran-fed chamber and a dextran-free chamber, and the osmotic pressure was measured (see Fig. 6). Although Ba^{2+} and Ca^{2+} diffuse in opposite directions, there was no concentration gradient of ions between the chambers. When Ba^{2+} was present in the dextran-fed chamber, the pores adjacent to the dextran solution closed while the pores adjacent to the dextran-free solution opened. In this case, osmotic pressure was generated as shown in Fig. 6(A). On the other hand, when Ca^{2+} was present in the dextran-fed chamber, the pores adjacent to the dextran solution opened and the pores adjacent to the dextran-free solution closed. In this case, osmotic pressure was almost 0 KPa, and then it gradually and slightly increased as shown in Fig. 6(B). The reason is that pores adjacent to the dextran solution opened, allowing the dextrans to diffuse through the pores, and an osmotic pressure could not be generated.

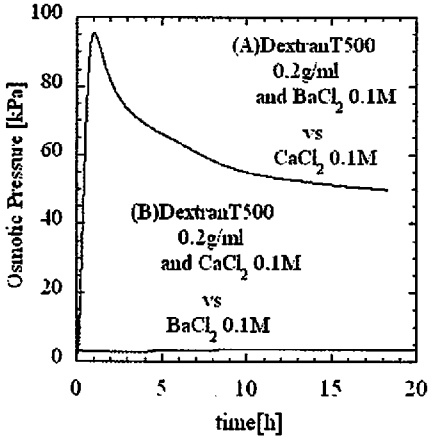

Figure 6. Time course of osmotic pressure in the counter diffusion of Ba^{2+} and Ca^{2+} through the gating membrane. The ion concentraioth gradient did not exist, however, Ba^{2+} was fed from solution chamber in the case of (A) . On the other hand, Ba^{2+} was fed fro solvent chamber in the case of (B).

4. CONCLUSIONS

A molecular recognition ion gating membrane comprising the copolymer of N-isopropylacrylamide and benzo[18]-crown-6-acrylamide grafted onto the surface of a porous polyethylene film was prepared and evaluated. We succeeded in generating osmotic pressures in response to both a temperature change and a specific ion signal. This was driven by the concentration gradient of another added polymer, such as dextran. Control of the membrane pore size is important to control these phenomena. A low grafting ratio did not generate an osmotic pressure. Furthermore, the ion concentration and its distribution in the gating membrane are

of crucial importance to the osmotic pressure generation.
In the future, these phenomena can be expected to be applied to novel sensors, affinity membranes, microfluid devices and drug delivery systems, amongst other applications.

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