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Relaxation of Polymer Chains Dissolved in the Liquid Phase of Membranes under a Pressure Gradient. III. Hydrogel Membranes of Poly(vinyl alcohol) and Poly(sodium L-glutamate)

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The dependence of the streaming potential across hydrogel membranes on time was measured. The gel membranes used were obtained by blending various amounts of poly(vinyl alcohol) and poly(sodium L-glutamate), which have different average molecular weights per cross-linked unit. The streaming potential increased rapidly just after applying a pressure difference and then increased gradually up to a steady-state value. The time dependence of the streaming potential was analyzed as the relaxation of the polymer chains dissolved in the liquid phase of the membrane. The relaxation for all the gel membranes consisted of a single component. The relaxation time was long if the gel had a large average molecular weight per cross-linked unit. The effects of cross-linking and the concentration of the external solution on the relaxation time are discussed.

When two solutions with the same composition and at the same temperature, but at different pressures, are separated by a membrane, an electric potential difference appears across the membrane. This electric potential difference is called a streaming potential.[1)] The streaming potential is known to depend on time when a polymer membrane is used.[2—5)] If a pressure difference is applied across a polymer membrane, the polymer chains dissolved in the liquid phase of the membrane are forced from the high pressure side to the low pressure side. Thus, the conformation of the polymer chains will change gradually with time, and finally reach a steady state. In previous papers,[4,5)] we have shown that the dependence of the streaming potential on time can be assigned to the relaxation of the polymer chains dissolved in the liquid phase of the membrane under a pressure gradient. Moreover, it was found that if the membrane is made of different kinds of polymer chains, the overall relaxation consisted of the sum of the relaxation components of their polymer chains. If more flexible and longer polymer chains were dissolved in the liquid phase, the relaxation time became longer. If a membrane which contained ionic sites was cross-linked by multivalent ions, the relaxation time measured became shorter than that for an uncross-linked membrane.[5)] However, there are very few quantitative studies concerning the relationships between the molecular weight per cross-linked unit of the polymer membranes and the relaxation time.

In this study, we measured the dependence of the streaming potential on time across hydrogel membranes obtained by blending poly(vinyl alcohol) and poly(sodium L-glutamate). By varying the initial contents of these components, the membranes had different molecular weights per cross-linked unit obtained from the measurements of the elastic modulus. The relationships between the relaxation time and the average molecular weight per cross-linked unit were studied quantitatively. The effects of cross-linking and the concentration of the external solution on the relaxation time are discussed.

Experimental

Membranes. Gel membranes used in this study were highly elastic, high-water-content hydrogel membranes obtained by blending concentrated aqueous solutions of poly(vinyl alcohol) (PVA) and poly(sodium L-glutamate) (PSLG) in an autoclave under a pressure of 200 kPa at 120 °C, and dehydration of the resulting coagulate followed by swelling. By varying the initial content of PVA and PSLG, hydrogel membranes PVA–PSLG 30, 50, 60, and 70 were prepared, where the number indicates the weight fraction of PSLG. The elastic modulus of the hydrogels increases with the initial content of PSLG. This is primarily due to the formation of rigid segments by the interaction of PVA chains with PSLG chains and formation of bound water. The average molecular weights per cross-linked unit obtained from the measurement of the elastic modulus were 1220, 1100, 1010, and 890 for PVA–PSLG 30, 50, 60, and 70, respectively. Other details were reported in Ref. 6. Some properties of these hydrogel membranes are listed in Table 1.

Measurements of Streaming Potential. A membrane was mounted between two 50 cm^3 compartments of a cell made of poly(vinyl chloride) and equipped with silver–silver chloride electrodes, a thermometer and joints to a pressurizing unit employing a hydrostatic pressure difference as described in the previous papers.[4,5)] The membrane area was 3.1 cm^2. The electrical potential difference across the membrane was measured with a vibrating reed electrometer (Takeda Riken TR-8411). The output signal from the electrometer was digitized through a digital multimeter(Takeda Riken TR-6841) and fed into a personal computer at intervals of 2 s. Measurements were carried out at 25 °C in an air-conditional thermostat. The bathing solution was 0.001 $\mathrm{mol\,kg^{-1}}$ NaCl solution, unless otherwise noted.

Results and Discussion

The streaming potential increased rapidly just after applying a pressure difference, and then increased grad-

Table 1. The Properties of Gel Membrane PVA–PSLG

Mambrane	Thickness mm	Water content g/g dry membr.	Molecular weight per cross-linked unit, M_{C}
PVA–PSLG 30	0.15	6.87	1220
50	0.37	4.90	1100
60	0.28	4.96	1010
70	0.25	4.96	890

ually up to a steady-state value. The steady-state value, $\Delta\psi(\infty)$, was plotted against the applied pressure difference, ΔP, for the gel membranes, PVA–PSLG 30, 50, 60, and 70, as shown in Fig. 1. Linear relationships were observed up to a pressure difference of 5.89 kPa for all the membranes. Therefore, the analysis of the streaming potential was carried out using the data measured at 5.89 kPa where the linear relationships hold.

The time dependences of the reduced streaming potentials, $\Delta\psi^{\mathrm{r}}(t)$, across the membranes, PVA–PSLG 30, 50, 60, and 70, are shown in Fig. 2. The reduced streaming potential at time t was defined by $\Delta\psi^{\mathrm{r}}(t)=\Delta\psi(t)/\Delta\psi(\infty)$, where $\Delta\psi(t)$ and $\Delta\psi(\infty)$ are the streaming potentials at time t and the steady state, respectively. The features approaching the steady-state values after switching the pressure difference from 0 to 5.89 kPa are different from each other.

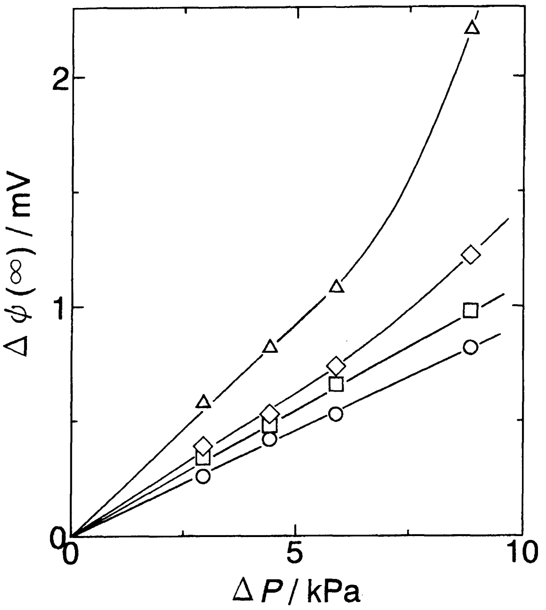

Fig. 1. The relationship between streaming potential at steady state, $\Delta\psi(\infty)$, and pressure difference applied, ΔP. Membranes; △, PVA–PSLG 30; ◇, PVA–PSLG 50; □, PVA–PSLG 60; ○, PVA–PSLG 70.

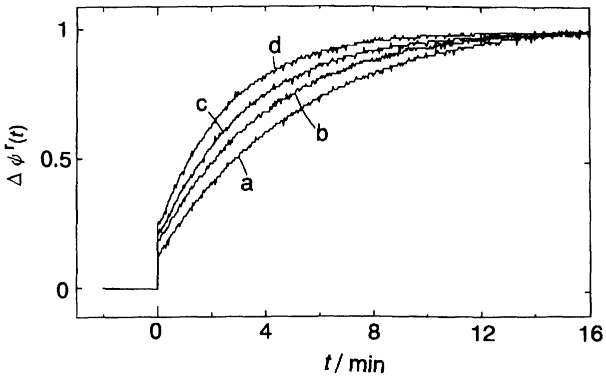

Fig. 2. The dependence of reduced streaming potential, $\Delta\psi^{\mathrm{r}}(t)$, on time. Membranes: a, PVA–PSLG 30; b, PVA–PSLG 50; c, PVA–PSLG 60; d, PVA–PSLG 70. Values of $\Delta\psi^{\mathrm{r}}(\infty)$/mV: a, 1.16; b, 0.72; c, 0.66; d, 0.51.

The dependence of the reduced streaming potential on time may be assigned to relaxation of the polymer chains under the pressure gradient. Therefore, the equation between the reduced streaming potential and time may be written as;

$$\Delta\psi^{\mathrm{r}}(t) - \Delta\psi^{\mathrm{r}}(\infty) = k\ \exp(-t/\tau) \tag{1}$$

and

$$\ln\mid \Delta\psi^{\mathrm{r}}(t) - \Delta\psi^{\mathrm{r}}(\infty)\mid = -t/\tau + K, \tag{2}$$

where $\Delta\psi^{\mathrm{r}}(\infty)$ is the reduced streaming potential at the steady state, τ the relaxation time, and k and K are constants.[4)]

Figure 3 shows the plots of $\ln|\Delta\psi^{\mathrm{r}}(t)-\Delta\psi^{\mathrm{r}}(\infty)|$ against time for these gel membranes. The straight lines were drawn by the least squares method. The relaxation times obtained from the slopes were 314, 258, 202, and 162 sec for PVA–PSLG 30, 50, 60, and 70, respectively. In the previous studies of the time depen-

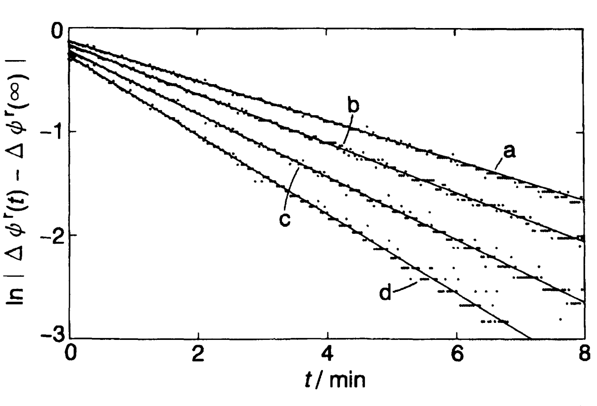

Fig. 3. The relationship between $\ln|\Delta\psi^{\mathrm{r}}(t)-\Delta\psi^{\mathrm{r}}(\infty)|$ and time. Symbols are the same as those in Fig. 2.

dence of the streaming potential for interpolymer membranes of collodion and poly(acrylic acid), the overall relaxation consisted of a few components, that is, the plots of $\ln|\Delta\psi^r(t)-\Delta\psi^r(\infty)|$ against time were composed of the sum of a few straight lines, which corresponded to the polymer chains in the membrane.[5] The present gel membrane, PVA–PSLG, consisted of two different components, PVA and PSLG, however, each plot of $\ln|\Delta\psi^r(t)-\Delta\psi^r(\infty)|$ against time was made of a simple straight line. This is because most of the PSLG chains involved interacted with PVA chains to make cross-linked points and polymer chains between these cross-linked points consisted mainly of amorphous PVA chains.[6,7] Figure 4 shows the dependence of the relaxation time on the average molecular weight per cross-linked unit in 0.01 and 0.001 mol kg^{-1} NaCl solutions. The relaxation time became longer with increasing average molecular weight per cross-linked unit. If the molecular weight per cross-linked unit becomes large, the degree of freedom of the polymer chains will be large. Thus, if the change in the conformation of the polymer chains under a pressure difference is large, the relaxation time becomes large to reach the steady-state conformation.

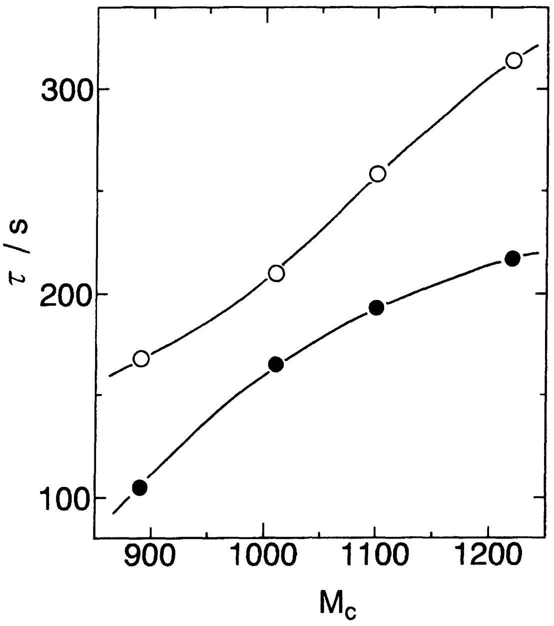

Fig. 4. The dependence of the relaxation time, τ, on the average molecular weight per cross-linked unit, M_C. Molality of the external NaCl solutions (mol kg^{-1}): ○, 0.001; ●, 0.01.

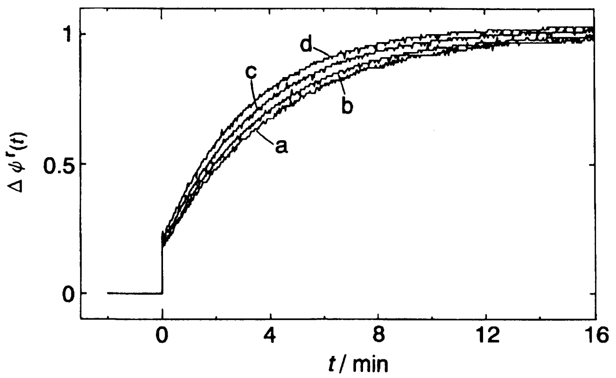

Fig. 5. The dependence of reduced streaming potential, $\Delta\psi^r(t)$, on time. Membranes: a, PVA–PSLG 50 (0); b, PVA–PSLG 50 (5); c, PVA–PSLG 50 (15); d, PVA–PSLG 50 (30), where the number in parenthesis represents time in minutes of electrodialysis through PVA–PSLG 50 in FeCl$_2$ solution. Values of $\Delta\psi(\infty)$/mV: a, 0.72; b, 0.68; c, 0.68; d, 0.64.

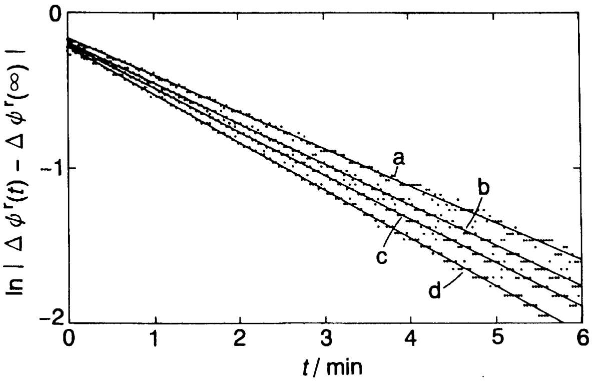

Fig. 6. The relationship between $\ln|\Delta\psi^r(t)-\Delta\psi^r(\infty)|$ and time. Symbols are the same as those in Fig. 5.

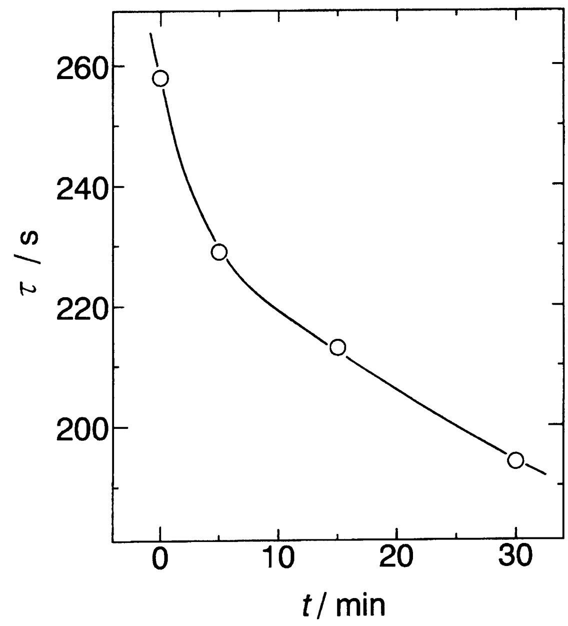

Fig. 7. The dependence of the relaxation time, τ, on time of electrodialysis in 0.001 mol kg^{-1} FeCl$_2$ solution.

The relaxation times measured in 0.01 mol kg^{-1} NaCl solution were shorter than those measured in 0.001 mol kg^{-1} NaCl solution. The molality of salt absorbed in a membrane increases when the molality of the external salt solution is increased. Therefore, the shield effect decreases the electrostatic repulsion among fixed charges due to the salt absorbed at higher salt molalities. The conformation of the polymer chains changes from an extended to a contracted one. As a result, the relaxation time becomes shorter in 0.01 $\mathrm{mol\,kg^{-1}}$ NaCl solution.

When poly(sodium L-glutamate) is cross-linked with Fe^{2+}, the structure of the gel membrane becomes more rigid and the average length of the chains for motion apparently becomes shorter. Thus, it is expected that the relaxation time will become shorter as the Fe^{2+} cross-linkages increase. Figure 5 shows the time dependence of the streaming potential across PVA–PSLG partially complexed with iron(II). The cross-linking was performed in 0.01 $\mathrm{mol\,dm^{-3}}$ $FeCl_2$ by electrodialysis at a current density 1.3 $\mathrm{mA\,cm^{-2}}$. The electrodialysis times were 5, 15, and 30 min for curves b, c, and d, respectively. Figure 6 shows the plots of $\ln|\Delta\psi^{\mathrm{r}}(t)-\Delta\psi^{\mathrm{r}}(\infty)|$ against time for these membranes. If the degree of cross-linking increases, the streaming potential reaches a steady-state value more rapidly because the freedom of movement of the polymer chains decreases. Figure 7 shows the dependence of the relaxation time on the electrodialysis time. As expected, the relaxation time became shorter with increasing time of electrodialysis. If the relationship between the relaxation time and the average molecular weight per cross-linked unit as shown in Fig. 1 holds for these cross-linked membranes, from the relaxation times of 258, 229, 213, and 194 s for membranes which were electrodialyzed for 0, 5, 15, and 30 min, the average molecular weights per cross-linked unit of the membranes could be estimated to about 1100, 1060, 1020, and 960, respectively.

Conclusions

The relationship between the relaxation times of the polymer chains in hydrogel membrane PVA–PSLG and the polymer average molecular weights per cross-linked unit was discussed. The overall relaxation for all the gel membranes consisted of a single component. The relaxation time became longer as the average molecular weight per cross-linked unit increased. With increasing degrees of cross-linking of the hydrogel membranes with Fe^{2+} ions, the average molecular weight per cross-linked unit of the membranes decreased and the relaxation time became shorter.

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