

Thermo- and pH-Responsive Poly(A-ProOMe)-graft-poly(AAc) Membrane for Selective Separation of Metal Ions

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We investigated the permeation behavior of Li, Co, and Ni ions through thermo- and pH-responsive gel membranes, which were prepared by γ -ray grafting of pH-responsive poly(acrylic acid) (poly(AAc)) onto a thermo-responsive polymer gel of acryloyl-L-proline methyl ester (A-ProOMe). Using 15% AAc grafted membranes, the permeation constants of Li ions are 2.8 and 3.5 times higher than those of Co and Ni ions in a pH 6.0 buffer solution at 30 °C. These ratios are two and three times higher than those of 5 and 43% grafted gel membranes, respectively. By comparison with the permeation of metal ions through the non-thermo-responsive porous polyethylene membranes grafted with AAc chains or random copolymer gel membranes (poly(A-ProOMe-co-AAc)), it is clear that the structure in which adjacent carboxyl groups of poly(AAc) are surrounded by thermo-responsive A-ProOMe matrix causes selective permeability of Li ion over Co and Ni ions. The distributions of Co and Ni ions in the microscopic structures clearly show that the structure consisting of flexible chains of the carboxyl groups grafted onto the thermo-response gel membrane plays a decisive role in the superior selective permeation of a Li ion.

KEY WORDS: Gel / Graft / Polymerization / Radiation / Metal / Permeation /

In recent years, there have been a plenty of attempts for developing environmentally responsive gels, which undergo discontinuous and reversible volume phase transitions in response to external stimuli such as temperature, pH, electric fields, and solvent composition, because of their potential applications in the fields of drug delivery, separation systems, chemomechanical actuators, and the like.^{1–6}

The gel membrane can be prepared by a radiation induced polymerization method, characterized by simultaneously occurring processes of polymerization and self-crosslinking in aqueous solution.^{7–9} Since these gels can be formed from monomers only without initiator, crosslinker, or accelerator, the radiation method for gel preparation can be applied, making possible the formation of a super-clean gel. In addition to gel preparation, graft copolymers consisting of both random and block structures can be easily synthesized through simultaneous or stepwise polymerization by radiation (Figure 1).

There were several reports about temperature- and pH-responsive polymers and only temperature responsive hydrogels.^{10,11} However, there have not been reported about both thermo- and pH-sensitive hydrogels to control permeation behavior of metal ions. Thus, we had reported the successful preparation of gel membranes with both thermo- and pH-sensitivities using the radiation technique.⁶

The gel membranes consisted of poly(acrylic acid) (poly(AAc) graft chains with $pK_a = 4.7$,¹¹ onto a poly(acryloyl-L-proline methyl ester (A-ProOMe)) gel membrane, which undergoes volume phase transition at around 14 °C (poly(A-ProOMe)-graft-poly(AAc)).^{12,13} The gel membrane composi-

tion of which 15% is AAc graft chain exhibited volume change in response to both temperature and pH-changes. It may be assumed that the permeability of metal ions through membranes can be controlled by changing the volume of both the hydrophobic (A-ProOMe) and hydrophilic (AAc) portions of the membrane, and thus, we attempted to use thermo- and pH-responsive membranes for selective metal separation. The preliminary results of the permeation behavior of metal ions through the gel membranes were described in our previous paper.⁶ However, details of metal ion permeation through the membranes such as permeation conditions, composition and micro structures of the gel membranes, and interactions with metal ions, have not been done. Thus, in this paper, we investigated the optimal molar ratio for the grafting of AAc and optimum conditions, such as temperature and pH, for selective permeation of metal ions (Li, Co, and Ni) through the membranes. An element of lithium is one of the important materials for a lithium battery as well as the fuel element of a nuclear fusion system. Therefore, the recycling of Li ions by new membrane separation in stead of current extraction using chemical reagents should become a very environment-friendly system. Since Li, Co, and Ni ions are used for a lithium battery, we have been first attempting the separation of Li ions from Co and Ni ions for a basic research to establish a new element recycling system. Furthermore, the effects of thermo-responsiveness and graft chains block structure of the membrane on the selective permeation was investigated by comparing with membranes with non-thermo responsive structure (porous polyethylene) and random copolymer gel membranes.¹⁴

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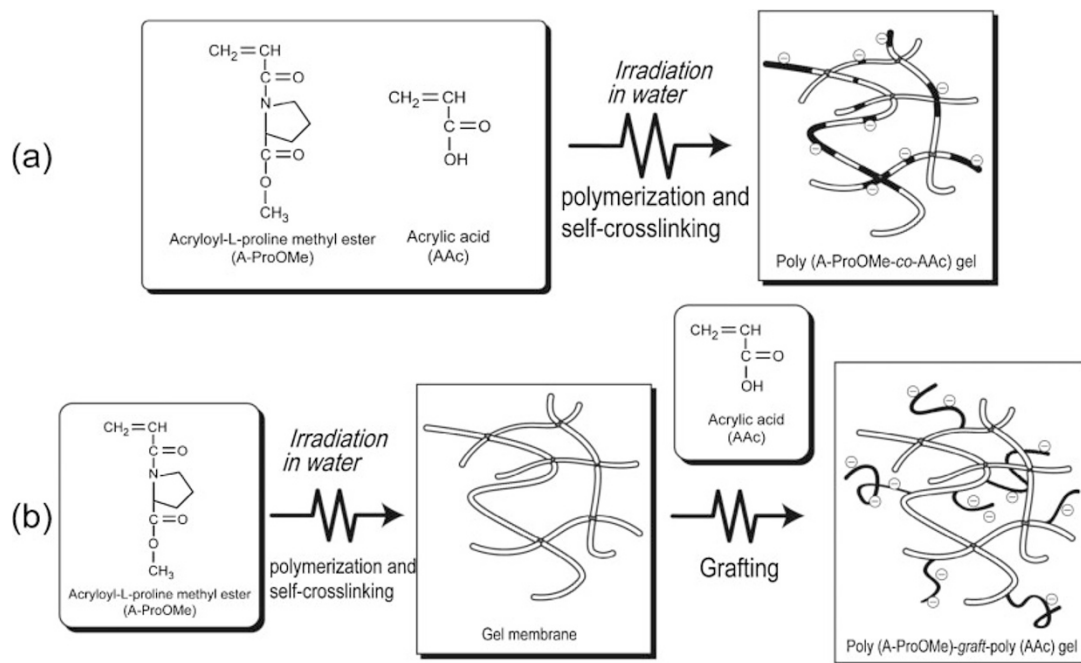


Figure 1. Schematic illustration for the synthesis of self-crosslinking random copolymer gels (a) and grafted block copolymer gels (b) using radiation technique.

EXPERIMENTAL

Materials

Acrylic acid (AAc; Kishida Chemical Co. Ltd.) was used after distillation. Distilled water (Kyoei Co Ltd.) and acetone (Wako Pure Chemical Co., Ltd.) were used as received. Lithium chloride anhydrous purchased from Kanto Chemical Inc. and cobalt chloride and nickel chloride purchased from Wako Pure Chemical Co., Ltd. were used without further purification. Buffer solutions of pH 1.0–9.0 consisting of potassium hydrogen phthalate and sodium hydroxide were purchased from Wako Pure Chemical Co., Ltd. and Kanto Chemical Inc., respectively. Acryloyl-L-proline methyl ester (A-ProOMe) was synthesized as described in previous papers.¹⁵ Graft copolymer gel membranes in response to change in temperature and pH were prepared in the same manners as described in previous paper.⁶

Synthesis of Copolymer Gel Membranes

Random copolymer gel membrane of AAc/A-ProOMe was synthesized as follows (Figure 2).^{14,15} The 30 vol. % aquarium mixture of AAc/A-ProOMe mole ratio (13:2 mol) was charged into two glass plates (50 × 50 × 2 mm) that was separated by an 800 μm poly(ethylene terephthalate) spacer film. The radiation-induced reaction for polymerization and crosslinking was carried out at 0 °C for 3 h at a dose rate of 10 kGy/h, using γ -rays from a ⁶⁰Co source. The obtained copolymer gels were washed with excess acetone and water to remove the unreacted monomer and homopolymers, and then displaced with water.

The graft polymerization was carried out in the same manner as previous reports.^{16,17} The porous poly(ethylene

(PE) films of 100 μm thickness (SUN MAP LC-T (NITTO DENKO CORPORATION)) were exhaustively rinsed by Soxhlet extractor in acetone for 24 h at 40 °C. The PE films were dried under vacuum and then were packed in a polyethylene bag under nitrogen atmosphere. Samples placed on a stainless-steel plate were irradiated with an electron accelerator (Dynamitron, Model IEA 300-25-2, Radiation Dynamics Co.) operating at beam energy of 2.0 MeV and a current of 1 mA at room temperature.

Immediately after irradiation, the porous films were placed into a glass ampoule and were evacuated. The introduction of AAc/acetone (90/10 vol. %) to those irradiated PE films was carried out under nitrogen atmosphere. The grafting was performed at 60 °C for 24 h. After grafting, the porous PE films were immersed in an excess amount of acetone, and gradually replaced into a distilled-deionized water to remove unreacted monomer and homopolymers. Subsequently, the films were dried under vacuum for 24 h. The grafting yield was calculated by the percentage increase in weight as follows:

$$\text{Degree of grafting (\%)} = 100 \times (W - W_0) / W_0$$

where W_0 and W represent the weight of initial and grafted films, respectively.

The Permeability Measurement

We measured the permeability constants (P) of metal ions through thermo- and pH-responsive gel membranes using a diffusion-type modified Franz cell.^{14,18} The gel membrane was cut into disks in 1.9 cm diameter and then set between two diffusion cells consisting of donor (5 mL) and receiver (50 mL) chambers, in which the effective film area was 2.83 cm². On metal permeation experiments through grafted gel membranes,

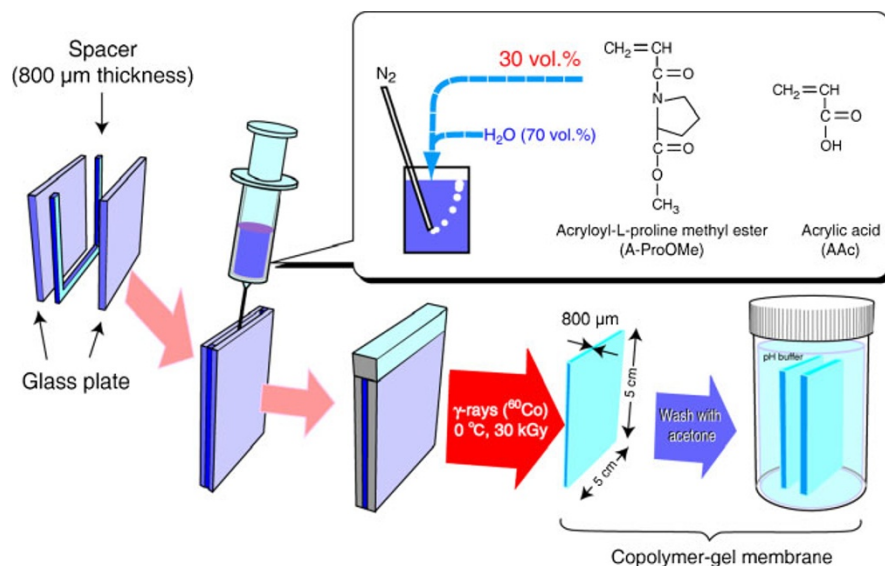


Figure 2. Schematic diagram for preparation of poly(A-ProOMe-co-AAc) gel membranes using radiation technique.

the gel membranes was sandwiched and tightly fixed with doughnuts type frosted glasses to suppress the dimensional change of the gel membranes caused by changes in pH, temperature, and the addition of metal ions. The initial concentrations of Li, Co, and Ni ions in the buffer solution prepared by potassium phthalate and sodium hydroxide were 0.01 mol. The cell set onto a stirrer (Iuchi M-3 multi-stirrer) that was immersed in a water thermostat. The mixed solutions of metal ions kept at 5 or 30 °C were charged into the donor chamber; the eluate of 1.0 mL of metal ion, which permeated from the donor to the receiver chambers through the grafted gel membrane, was collected from a sampling port at various intervals. The same volume of the buffer solution was immediately added to the receiver chamber. The eluate was diluted with distilled water to adjust the solution concentrations ranging from 0.1 to 10 ppb. The concentrations of Li, Ni, and Co ions that permeated the grafted gel membranes were determined quantitatively using an inductively coupled plasma mass spectrometer (ICP-mass, Hewlett Packard 4500SERIES). Each concentration was calibrated by the supplied standard solution (ICP-Multi-element standard solution IV (1 mol/L HNO₃)) purchased from SPEX Certi Prep. Inc.

Microscopic Observation

The physical structures of thermo- and pH-sensitive gel membranes were observed by using a scanning electron microscopy (SEM). The gel membrane with the fixed conditions of temperatures and pHs were immersed quickly into glass vessels previously cooled at -85 °C, kept on more than 6 h, and then lyophilized.¹⁹ The cross-section of the gel after coating with gold was observed with a JEOL JSM-5600 SEM. The concentration profile of Co and Ni ions bound across the thickness of the membrane, which is immersed in mixed solution of 0.01 mmol Li, Co, and Ni ions in a pH 6.0 solution at 30 °C, were determined using an energy-dispersive X-ray

spectroscopy (EDS) (model 7388) with Oxford Instruments INCA energy.

RESULTS AND DISCUSSION

The Effects of Graft Chains on Selective Permeation of Li Ions

Thermo- and pH-sensitive gel membranes were synthesized by γ -ray grafting of pH-responsive poly acrylic acid (poly-AAc) onto the thermo-responsive polymer gel acryloyl-L-proline methyl ester (A-ProOMe). In this paper, the graft degree of poly(AAc) is expressed as “X% grafted gel membrane,” where X% is defined by the following equation:

$$X\% = 100 \times \frac{\text{AAc}}{\text{in grafted gel (mol)/poly(A-ProOMe) gel (mol)}}$$

We successfully prepared three grafted gel membranes; a 5% grafted gel membrane exhibiting only thermo-sensitive volume, a 15% grafted gel membrane exhibiting both temperature and pH responses, and a 43% grafted gel membrane exhibiting only pH response.

The permeation ratios (M_t/M_∞) of Li, Co, and Ni ions through the 5, 15, and 43% grafted gel membranes are plotted as a function of time in pH 6.0 buffer solution at 30 °C in Figure 3, where M_t and M_∞ are defined as the amount of the ions permeating up to time t and up to infinite time ∞ , respectively.^{20–22} In those conditions, the M_t/M_∞ of Li ions through 5, 15, and 43% grafted gel membranes increased with the increase of time, reaching 0.12, 0.45, and 0.58, respectively after 10 h. Over the same period, the M_t/M_∞ of Co and Ni ions reached only about one third of those of Li ions.

For quantitative comparison of the permeation rates of metal ions through membranes, the initial permeation constant (P ($\times 10^{-4}$ mmol/L·min)) of each metal ion is defined as the maximum penetration rate the maximum change in permeation

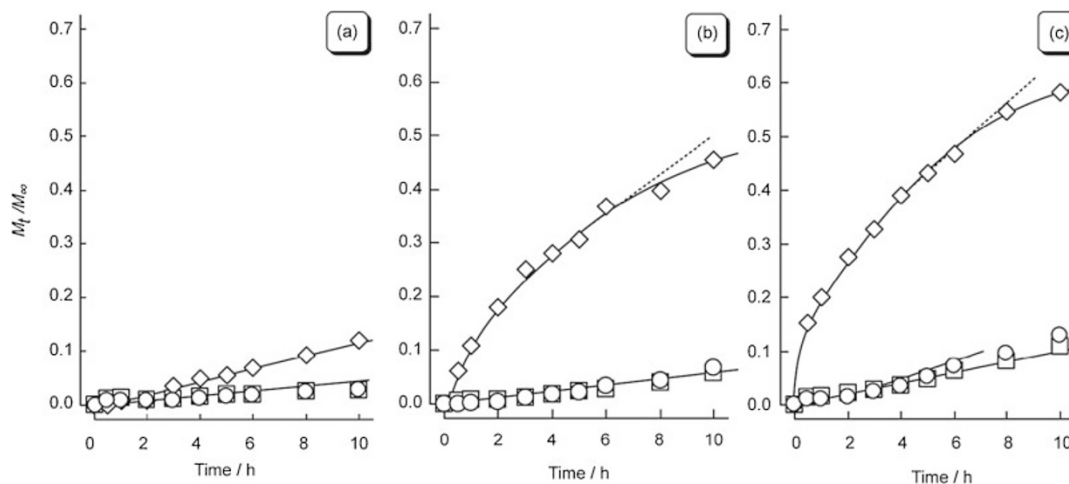


Figure 3. Plots of the permeation ratios (M_t/M_∞) of Li (\diamond), Co (\square), and Ni (\circ) ions through the gel membranes as a function of permeation time in a pH 6.0 buffer solution at 30 °C: 5% (a), 15% (b), and 43% (c) grafted gel membranes.

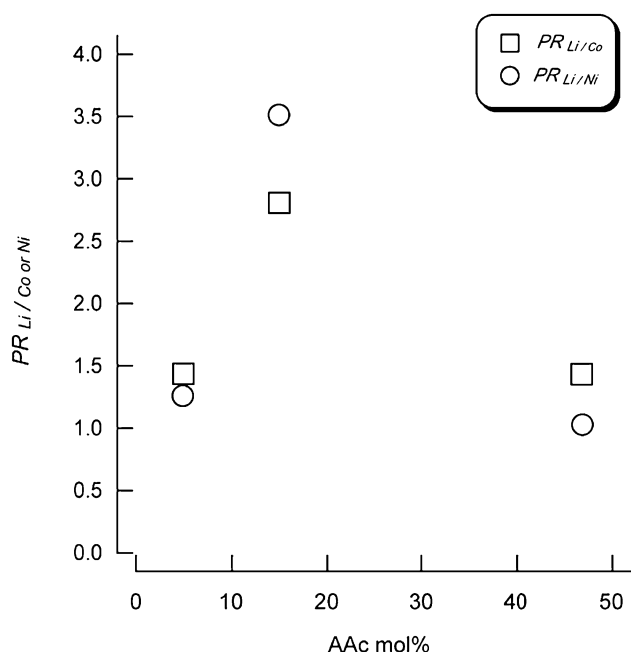


Figure 4. Plots of initial permeation rate ratios of Li/Co ions ($PR_{Li/Co}$, \square) and Li/Ni ions ($PR_{Li/Ni}$, \circ) through the gel membranes as a function of grafting degree of AAc in a pH 6.0 buffer solution at 30 °C.

concentration (mmol/L) per unit of time (minutes) (dM_t/dt) max, because M_t as a function of time exhibited an induction period for all the membranes. Then, the selective Li ion permeability over Co and Ni ions is expressed as the permeation rate ratios of Li/Co ions and Li/Ni ions ($PR_{Li/Co}$ and $PR_{Li/Ni}$) and are plotted as a function of AAc mol% in Figure 4. The 15% grafted gel membranes showed $PR_{Li/Co}$ and $PR_{Li/Ni}$ of 2.8 and 3.5, respectively. On the other hand, the 5 and 43% grafted gel membranes showed much smaller $PR_{Li/Co}$ (1.4 and 1.4) and $PR_{Li/Ni}$ (1.3 and 1.0) compared with the 15% grafted gel membrane. The difference is clearly explained from the results previously described in Figure 3. Namely, the

permeation rates of all the metals are very low in the 5% grafted gel membrane due to lack of ion conducting channels consisting of AAc grafts. On the contrary, 43% grafted gel membranes exhibited higher permeation rates of Ni and Co than those of 15% gel membrane, resulting in lower $PR_{Li/Co}$ (1.4) and $PR_{Li/Ni}$ (1.0). Since the 15% grafted gel membrane had greater $PR_{Li/Co}$ and $PR_{Li/Ni}$, 2.8 and 3.5, respectively, than those of 5 and 43% grafted gel membranes, the 15% grafted gel membrane was employed for the following permeation experiment.

Thermo- and pH-Responses of 15% Grafted Gel Membrane

The equilibrium swelling of the 15% grafted gel membrane is plotted as a function of pH in the range of pH 1.0–8.0 at 5, 10, 20, 30 and 60 °C in Figure 5. In a solution with acidity fixed at pH 4.0, the carboxyl groups of the AAc graft chains were deionized (-COOH), and the swelling ratio of the 15% grafted gel membrane decreased from 2.5 (open circle) to 0.2 (open diamond) with increases of temperatures from 5 to 30 °C. In a pH 6.0 buffer solution, the carboxyl groups of the AAc graft chains were ionized (-COO⁻), and the swelling ratio of the 15% grafted gel membrane also decreased from 8.5 (open circle) to 3.5 (open diamond) with increases of temperatures from 5 to 30 °C. With temperature fixed at 5 °C, at which the poly(A-ProOMe) moiety is in a swollen state, the volume ratios in the 15% grafted gel membrane increased from 2.5 to 8.5 with increases of the acidity from pH 4.0 to 6.0. In a buffer solution at 30 °C, at which the poly(A-ProOMe) moiety is in a shrunken state, the volume ratios of the 15% grafted gel membrane increased from 0.22 to 3.5 with increases of the acidity from pH 4.0 to 6.0. It is clear from above observations that the volume of the 15% grafted gel membrane can be controlled by changing in temperature and pH of the buffer solution. The pH break points, above which the gel membranes start swelling, were shifted from pH 4.5 to 5.0 when the gel membranes placed above 30 °C. This shift should result from

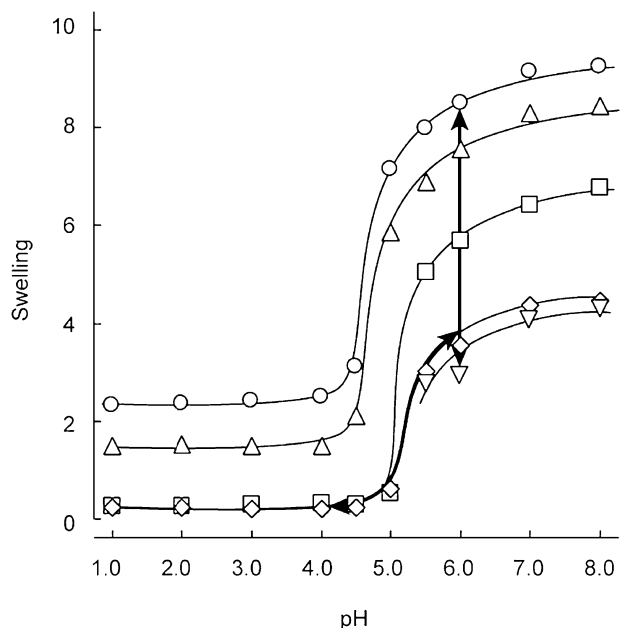


Figure 5. The equilibrium swelling of the 15% poly(A-ProOMe)-graft-poly(AAc) gel membrane as a function of pH in the range of pH 1.0–9.0 at the temperatures of 5°C (○), 10°C (△), 20°C (□), 30°C (◇), and 60°C (▽).

the suppress of swelling in ionizing poly(AAc) moiety surrounded by the deswollen thermo-responsive (A-ProOMe) moiety.

Thermo- and pH-Effects of Permeation of Li Ions through the 15% Gel Membrane

The selective Li ion permeability over Co and Ni ions of the 15% grafted gel membrane, $PR_{Li/Co}$ and $PR_{Li/Ni}$ were plotted in Figure 6 as functions of temperature in the fixed acidity of pH 6.0. At 5 °C in the pH 6.0 buffer solution, in which both thermo-responsive A-ProOMe membranes and pH responsive poly(AAc) were in swollen states, the selective Li ion permeability over Co and Ni ions through the membranes were not very high ($PR_{Li/Co} = 2.2$ and $PR_{Li/Ni} = 1.1$). When the temperature increased to 30 °C, at which the thermo-responsive unit deswelled and the pH responsive unit remains to swell, the selectivity of Li permeation increased to $PR_{Li/Co} = 2.8$ and $PR_{Li/Ni} = 3.5$. However, at 60 °C, the membrane, which has the same swollen and deswollen structures as that at 30 °C, showed lower $PR_{Li/Co}$ and $PR_{Li/Ni}$ (0.84 and 0.87) than those at 30 °C. The trend of the $PR_{Li/Co}$ and $PR_{Li/Ni}$ values of the 15% grafted gel membranes at 5 and 30 °C seems to be reverse order to each other in Figure 6. However, this is probably due to the very low permeation rates (0.84 and 0.87 mmol/l min) at 60 °C. On the other hand, similar $PR_{Li/Co}$ and $PR_{Li/Ni}$ values of the 15% grafted gel membrane at 5 °C can be explained by the fact that the permeation rates of both Ni and Co ions are too high to show a selective PR to each other, resulting in more error values at 5 °C.

Figure 7 shows the plots of $PR_{Li/Co}$ and $PR_{Li/Ni}$ as functions of pH at the fixed temperature of 30 °C. The selective Li ion

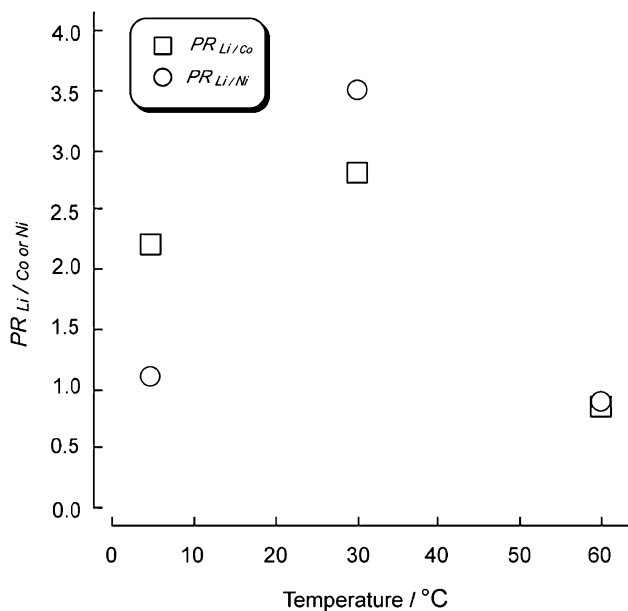


Figure 6. Plots of initial permeation rate ratios of Li/Co ions ($PR_{Li/Co}$, □) and Li/Ni ions ($PR_{Li/Ni}$, ○) of 15% grafted gel membranes as a function of temperature in a pH 6.0 buffer solution.

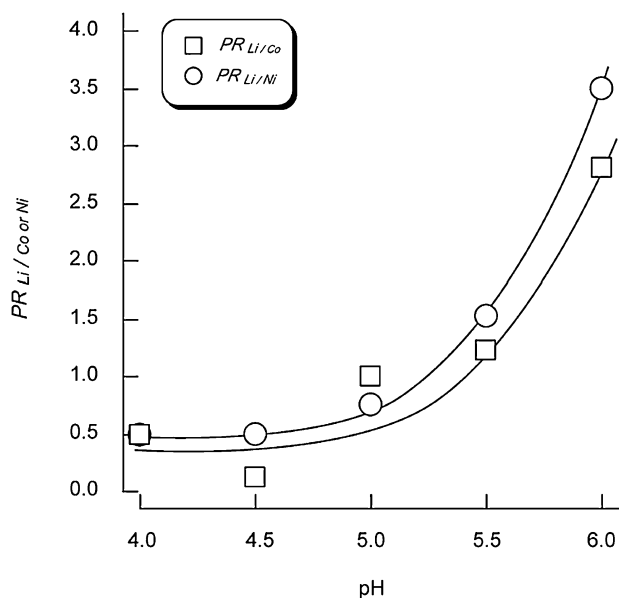


Figure 7. Plots of permeation rate ratios of Li/Co ions ($PR_{Li/Co}$, □) and Li/Ni ions ($PR_{Li/Ni}$, ○) of 15% grafted gel membranes as a function of pH at 30 °C.

permeability over Co and Ni ions ($PR_{Li/Co}$ and $PR_{Li/Ni}$) at pH 4.0 were 0.50 and 0.50, respectively. When the pH of the buffer solution increased to pH 6.0, $PR_{Li/Co}$ and $PR_{Li/Ni}$ increased gradually and reached to 2.8 and 3.5 at pH 6.0, at which the thermo-responsive unit deswelled and the pH-responsive unit swelled, respectively. Unfortunately, the membranes are not mechanically strong enough in the pH above 7.0. Consequently, it is clear that the optimal condition for the selective permeation of Li ions through the 15% grafted gel membrane were at 30 °C in a pH 6.0 buffer solution.

Table I. Permeation constants (P) and permeation constant ratios (PR) of PE-*graft*-poly(AAc) and poly(A-ProOMe-*co*-AAc) gel membranes (P : $\times 10^{-4}$ mmol/L-min)

	Permeation constants			Permeation constant ratios	
	P_{Li}	P_{Co}	P_{Ni}	$PR_{\text{Li/Co}}$	$PR_{\text{Li/Ni}}$
PE- <i>graft</i> -poly(AAc)	4.0	1.9	1.4	2.1	2.9
poly(A-ProOMe- <i>co</i> -AAc)	5.2	3.9	3.4	1.3	1.5

Effect of Thermo-responsive Matrix and pH Sensitive Grafted Chain Structures

The effect of thermo-responsive poly(A-ProOMe) gel matrix on the selective Li ion permeability over Co and Ni ions through the grafted gel membrane should be evaluated by comparing the selective permeation characters with the membranes consisting of AAc graft chains on porous polyethylene membranes (PE-*graft*-poly(AAc)) that are not thermo-responsive. 74% grafted PE-*graft*-poly(AAc) was synthesized by grafting AAc onto PE porous film because the 74% grafted membranes shows almost the same initial permeation rate of Li ions ($4.0 \times 10^{-4} \text{ min}^{-1}$) as that of 15% poly(A-ProOMe)-*graft*-poly(AAc) ($5.6 \times 10^{-4} \text{ min}^{-1}$). The selective Li ion permeability over Co and Ni ions through PE-*graft*-poly(AAc) membrane ($P_{\text{Li}} = 4.0$) at 30 °C in pH 6.0 buffer solutions was higher than those of Co ($P_{\text{Co}} = 1.9$) and Ni ($P_{\text{Ni}} = 1.4$), respectively (Table I). However, the selective Li ion permeability over Co and Ni ions, $PR_{\text{Li/Co}}$ (2.1) and $PR_{\text{Li/Ni}}$ (2.9) of the PE grafted membrane were lower than those of the 15% grafted gel membrane (about 80%). Accordingly, the thermo-responsive poly(A-ProOMe) makes a condition to the selective permeation of Li ions over Co and Ni ions.

Next, we investigated the effect of the AAc configuration in the gel membranes (block and random structures) on the selective Li ion permeability over Co and Ni ions. A random copolymer gel membrane, in which 15% AAc are dispersed in a main chain of poly(A-ProOMe), were synthesized; then, the selective Li ion permeability over Co and Ni ions ($PR_{\text{Li/Co}}$ and $PR_{\text{Li/Ni}}$) were compared with those of the 15% grafted poly(A-ProOMe)-*graft*-poly(AAc). The random copolymer gel membrane of AAc and A-ProOMe (poly(A-ProOMe-*co*-AAc)) was synthesized at 0 °C for 3 h at a dose rate of 10 kGy/h, using γ -rays from a ^{60}Co source. The permeation of Li ions (P_{Li}) through poly(A-ProOMe-*co*-AAc) gel membrane in a pH 6.0 buffer solutions at 30 °C was 5.2, which is slightly higher than those of Co and Ni ions (3.9 and 3.4) (Table). However, the selective Li ion permeability over Co and Ni ions $PR_{\text{Li/Co}}$ (1.3) and $PR_{\text{Li/Ni}}$ (1.5) of the copolymer were only 37–53% of those of the 15% grafted gel membrane. In general, a block-type graft copolymer retains the chemical and physical properties of the corresponding homopolymers, while random co-polymers exhibit the different properties of each homopolymer.⁶ Accordingly, the branched structure of the carboxyl groups of poly(AAc) surrounded by thermo-response A-ProOMe matrix is required for the selective interactions with Co and Ni, resulting in faster ion permeability of Li over Co and Ni ions.

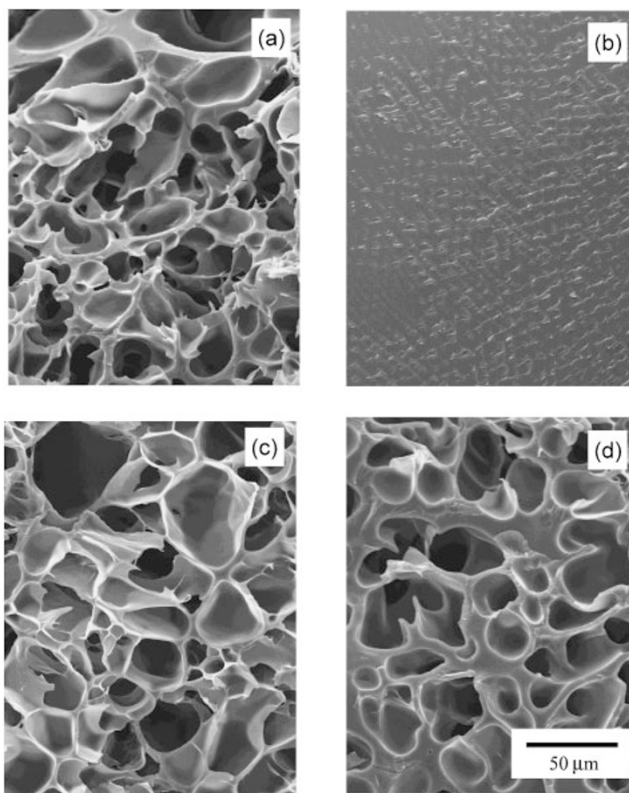


Figure 8. Cross-sectional SEM photographs of 15% poly(A-ProOMe)-*graft*-poly(AAc) gel membranes at various conditions; 5 °C/pH 4.0 (a), 30 °C/pH 4.0 (b), 5 °C/pH 6.0 (c), and 30 °C/pH 6.0 (d).

Microscopic Structures Observed by SEM

To find the relation between micro porous structures of gel membranes and the selective permeability of Li ions, the microscopic network structures in the grafted gel membranes were investigated using a scanning electron microscopy (SEM). The cross-sectional photographs of the gel membranes A, B, C, and D, which were kept under the conditions 5 °C/pH 4.0, 30 °C/pH 4.0, 5 °C/pH 6.0, and 30 °C/pH 6.0, and then lyophilized, are shown in Figure 8(a)–(d). The A-ProOMe matrix and AAc graft chains of gel membranes A, B, C, and D are in the swollen/shrunk, shrunken/shrunk, swollen/swollen, and shrunken/swollen states, respectively. The gel membrane B found in a pH 4.0 buffer solution at 30 °C does not show any metal permeation selectivity, due to complete shrinkage of both matrix and grafted chains, as shown in Figure 8(b). The gel membrane C formed in a pH 6.0 buffer solution at 5 °C, which exhibits less metal ion permeation selectivity, has thinner walls and larger pore size, as shown in Figure 8(c). The micro-structure of the gel membranes A and D are similar to each other; both membranes have thick walls with pores. The porous structure in the gel membrane A should consist of the shrunken poly(AAc) graft chains as a thick wall (about 2.1 μm), whereas that in the gel membrane D should consist of the shrunken A-ProOMe matrix as a thick wall (about 6.4 μm). These gel structure observations strongly suggest that the gel micro-structure consisting of ion channels

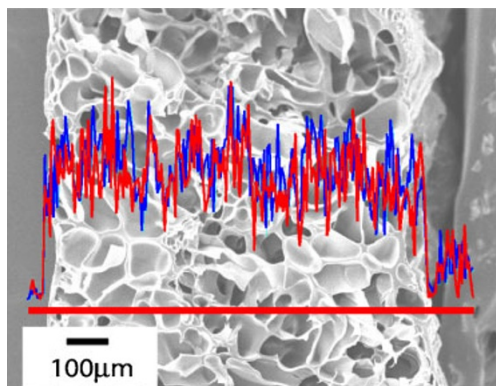


Figure 9. EDS profiles of Co and Ni ions across the 15% poly(A-ProOMe)-graft-poly(AAc) gel membrane after 10 h of permeation experiment in a pH 6.0 buffer solution at 30 °C (Red line: Co, Blue line: Ni).

of poly(AAc) grafted chains separated by a thicker wall of A-ProOMe is a favorable for the selective permeation of metal ions.

When we continued permeation experiments of the of Li, Co and Ni ions through the 15% poly(A-ProOMe)-graft-poly(AAc) gel membrane in a pH 6.0 buffer solution at 30 °C, the permeation of Li ions started immediately after the beginning of the experiment and achieved equilibrium at 24 h. In contrast, the permeation of Co and Ni ions exhibited an induction period of 2 h and the permeation rates of these metal ions did not level off even after 60 h. Figure 9 shows the distributions of Co and Ni ions along the cross section of the graft gel membrane, which was measured by the line scan of an energy-dispersive X-ray spectroscopy (EDS), after 10 h of permeation. Co and Ni ions were distributed along the cross section of the membrane from the source to the receiver sides, as shown in Figure 9. The concentration profile of Co and Ni ions is not homogeneous, since the permeation rate should be zero. However, the concentration gradient of the metal ions in the membranes should be too small to be detected by SEM-EDS measurement.

On the basis of the above results, the Li-selective permeation can be interpreted as follows. The induction period observed for only Ni and Co ions results from the larger interactions of Ni and Co ions with the carboxylic groups in the grafting chains compared with that of Li ions. Co and Ni ions form complexes with carboxylate anions of the acrylic acid-grafted chains in the 15%-grafted membrane just after the permeation. It is well known that the multi functional carboxylic acids have strong affinity to polyvalent metal ions such as Co and Ni than monovalent one even though acetic acid does not show such selectivity.²³ For example, ETDA, which has four carboxylic acids, shows 16.3 and 18.6 of binding constants with Co and Ni, which is much higher than that with Li (2.8).²³ By taking account of the results that block but random copolymer gel membrane can exhibit selective permeation of Li ions, adjacent carboxyl groups of poly(AAc) on the thermo-responsive walls can make suitable conformation to interact with Co and Ni ions by the four coordinate structure. The pore sizes of ion channels (21–35 μm) of

poly(AAc) graft chains constructed by the A-ProOMe walls are much larger than the diameters of hydrated Co and Ni ions (0.4 nm). Thus, it is obvious that the pore and wall structures constructed by pH and thermo-responsive polymers are not suitable for size recognition of hydrated metal ions but allow the poly(AAc) graft chains on the A-ProOMe walls to take suitable conformation to interact with Co and Ni ions by the four coordinate structure.

Co and Ni ions gradually diffuse into the membrane and after 2 h, they start permeating through the other side of membrane and the complexation reaches equilibrium. After this equilibrium state, the Co and Ni ions slowly permeate through, repeating dissociation and complexation with carboxylate ions along a graft chain or between graft chains. On the other hand, Li ions can permeate quickly without the complexation with carboxyl anions. As a result, the selective permeation of Li over Co and Ni ions through the 15% grafted gel membrane can be achieved in a pH 6.0 buffer solution at 30 °C.

CONCLUSIONS

We investigated the permeation behavior of Li, Co, and Ni ions through thermo- and pH-responsive gel membranes. The gel membranes were synthesized by γ -ray grafting of pH-responsive poly(acrylic acid) (AAc) onto a thermo-responsive polymer gel of acryloyl-L-proline methyl ester (A-ProOMe). Using 15% AAc grafted membrane, the permeation constant of Li ions through the membrane is 3.5 and 2.8 times higher than those of Co and Ni ions in a pH 6.0 buffer solution at 30 °C. These ratios are two and three times higher than those of 5 or 43% grafted gel membranes, respectively. By comparison with the permeation of metal ions through the grafted membranes consisting of AAc graft chains on porous polyethylene membranes (PE-graft-poly(AAc)) that are not thermo-responsive as well as that of a random copolymer gel (poly(A-ProOMe-co-AAc)), it is clear that both adjacent chains of the block structure, in which the carboxyl groups of poly(AAc) surround by thermo-responsive A-ProOMe matrix appear be essential for the selective Li ion permeability over Co and Ni ions. From the microscopic structures in the gel membranes (SEM) and the distributions of Co and Ni ions (EDS), we confirmed that the gel structures formed by the flexible grafted chains of the carboxyl groups onto the thermo-response gel membrane play a decisive role for the selective permeation of Li over Co and Ni ions.

Received: November 22, 2007

Accepted: March 19, 2009

Published: May 13, 2009

REFERENCES

1. F. Martellini, O. Z. Higa, E. Takacs, A. Safranji, M. Yoshida, R. Katakai, and M. Carena, *Radiat. Phys. Chem.*, **55**, 185 (1999).
2. M. Yoshida, A. Safranji, H. Omichi, and R. Katakai, *Radiat. Phys. Chem.*, **46**, 1053 (1995).

3. J. Chen, S. Hasegawa, H. Ohashi, Y. Maekawa, M. Yoshida, R. Katakai, and N. Tsubokawa, *Macromol. Rapid Commun.*, **23**, 141 (2002).
4. R. Yoshida, K. Sakai, T. Okano, and Y. Sakurai, *Adv. Drug Delivery Rev.*, **11**, 85 (1993).
5. Y. Osada, H. Okuzaki, and H. Hori, *Nature*, **355**, 242 (1992).
6. S. Hasegawa, H. Ohashi, Y. Maekawa, R. Katakai, and M. Yoshida, *Radiat. Phys. Chem.*, **72**, 595 (2005).
7. A. Hiroki, Y. Maekawa, M. Yoshida, and R. Katakai, *Polymer*, **42**, 6403 (2001).
8. N. Nagaoka, A. Safranji, M. Yoshida, and H. Omichi, *Macromolecules*, **26**, 7386 (1993).
9. M. Yoshida, A. Safranji, and H. Omichi, *Macromolecules*, **29**, 2321 (1996).
10. G. Chen and A. S. Hoffman, *Macromol. Rapid Commun.*, **16**, 175 (1995).
11. M. Higa and T. Yamakawa, *J. Phys. Chem. B*, **108**, 16703 (2004).
12. M. Yoshida, A. Safranji, H. Omichi, M. Miyajima, and R. Katakai, *Radiat. Phys. Chem.*, **46**, 181 (1995).
13. M. Yoshida, H. Omichi, H. Kubota, and R. Katakai, *J. Intell. Mater. Syst. Struct.*, **4**, 223 (1993).
14. J. Hendri, A. Hiroki, Y. Maekawa, M. Yoshida, and R. Katakai, *Radiat. Phys. Chem.*, **60**, 617 (2001).
15. M. Yoshida, H. Omichi, and R. Katakai, *Eur. Polym. J.*, **28**, 1141 (1992).
16. S. Tsuneda, K. Saito, S. Furusaki, and T. Sugo, *J. Chromatogr., A*, **689**, 211 (1995).
17. M. Kim and K. Saito, *Radiat. Phys. Chem.*, **57**, 167 (2000).
18. T. J. Franz, *J. Invest. Dermatol.*, **64**, 190 (1975).
19. N. Kato and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **70**, 1289 (1997).
20. M. Yoshida, M. Asano, T. Suwa, and R. Katakai, *Radiat. Phys. Chem.*, **55**, 677 (1999).
21. M. T. am Ende and N. A. Peppas, *J. Controlled Release*, **48**, 47 (1997).
22. W. Lee and R. Chiu, *J. Appl. Polym. Sci.*, **86**, 1592 (2002).
23. A. Ringbom, "Complexation in Analytical Chemistry," John Wiley and Sons Inc., New York, 1963.