

# Adsorption and Desorption Properties of Grafted Polyethylene Films Modified with Polyethylenimine Chains

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**ABSTRACT:** The chelating membranes for adsorption of metal ions were prepared by the bonding of linear and branched polyethylenimines (LPEI and BPEI) on the glycidyl methacrylate (GMA) photografted porous polyethylene (pPE) (pPE-g-PGMA) films. The adsorption and desorption properties of LPEI and BPEI-bonded pPE-g-PGMA (LPEI-(pPE-g-PGMA) and (BPEI-(pPE-g-PGMA))) films to  $\text{Cu}^{2+}$  ions were investigated as a function of the grafted amount, amount of bonded PEI, molecular mass of PEI, pH value, and temperature. The amounts of LPEI and BPEI bonded to the pPE-g-PGMA films increased over the reaction time, and the bonding of LPEI and BPEI offered the water-absorptivity to the pPE-g-PGMA films. The amount of adsorbed  $\text{Cu}^{2+}$  ions at pH 5.0 had the maximum value at the grafted amount of 10 mmol/g for the (LDPEI-(pPE-g-PGMA) and (BPEI-(pPE-g-PGMA))) films with a constant amount of bonded PEI. The amount of adsorbed  $\text{Cu}^{2+}$  ions

for the LPEI-(pPE-g-PGMA) films was higher than that for the BPEI-(pPE-g-PGMA) films. The amount of  $\text{Cu}^{2+}$  ions desorbed from the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films increased with an increase in the HCl concentration. The quantities of  $\text{Cu}^{2+}$  ions of about 100% were desorbed in the aqueous HCl solutions of more than 0.1M for the LPEI-(pPE-g-PGMA) films and more than 0.05M for the BPEI-(pPE-g-PGMA) films. The amounts of adsorbed  $\text{Cu}^{2+}$  ions were almost the same in each adsorption process at pH 5.0. This indicates that the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films can be applied to a repeatedly generative chelating membrane for adsorption and desorption of metal ions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5965–5976, 2006

**Key words:** polyethylene; photografting; glycidyl methacrylate; polyethylenimine; adsorption; desorption

## INTRODUCTION

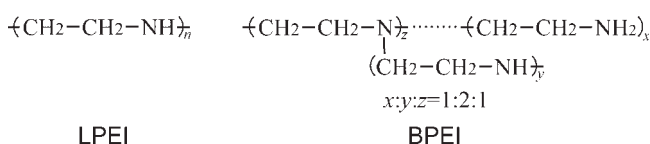
The UV-induced grafting technique and frequently subsequent functionalization<sup>1–3</sup> have been mainly used to modify the generally used polymer membranes such as polyethylene (PE), polypropylene, and porous and expanded polytetrafluoroethylene (pPTFE and ePTFE) films because these modification techniques make it easy to control the active sites for the formation of grafted polymer chains and the density of functional groups in the modified polymer substrates.<sup>4–7</sup> A variety of functional membranes with practical strength have been prepared by the photograftings of functional or reactive monomers throughout the PE films.<sup>4,8,9</sup> For more than one decade, our progressive work has been geared toward studying the application of the grafted PE and ePTFE films to the functional membranes for permeation control,<sup>4</sup> separation,<sup>10</sup> concentration,<sup>4,9</sup> and adsorption of vari-

ous ionic compounds in response to the temperature,<sup>4</sup> pH value,<sup>4,9</sup> and electrical field.<sup>5,9</sup> The introduction of an ion-exchange group or an affinity ligand to insoluble support materials enables us to remove various undesirable ions from wastewater.<sup>11</sup> Recently, the necessity for recovery and removal processes of heavy metal ions and the subsequent reuse of them have led to an increasing interest in preventing the environmental pollution and resource depletion.

Many researchers have reported removal of metal ions by adsorption on the chelating membranes,<sup>1–3</sup> fibers,<sup>12</sup> and beads or resins.<sup>13–19</sup> However, little was reported on the dependence of the metal ion adsorption on the chelating-functional group density, pH value, and temperature and the cyclic adsorption-desorption process for their reuse.<sup>18,20,21</sup> In many studies, reactive monomers such as acrylic acid (AA),<sup>2</sup> glycidyl methacrylate (GMA),<sup>15–17</sup> and styrene<sup>13,17</sup> were copolymerized with hydrophobic monomers in the presence of a bifunctional crosslinker, and then the chelate-forming functional groups were introduced to the resultant membranes or beads. In our previous paper, the chelating membranes for adsorption of metal ions were prepared by the photografting of GMA onto the PE films and the subsequent modifica-

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**Figure 1** Chemical structure of LPEI and BPEI.

tion of the GMA-grafted PE (PE-g-PGMA) films with disodium iminodiacetate. The iminodiacetate group-appended PE-g-PGMA films were applied to a repeatedly generative chelating membrane for adsorption and desorption of metal ions.<sup>22</sup> A membrane system has become a practical alternative to the bead system conventionally used for adsorption and separation in facile handling.

Here, we focused attention on the fact that the amino group containing polymers such as polyethylenimine (PEI), polyallylamine (PAAm), and polyvinylamine (PVAm) had high affinity for metal ions.<sup>18,23–25</sup> In addition, PEI falls into linear PEI (LPEI) with only secondary amino groups and highly branched PEI (BPEI) containing primary, secondary and tertiary amino groups in the ratio of 1 : 2 : 1 as shown in Figure 1. BPEI is used in most of the articles on adsorption of metal ions on the membranes and beads prepared or modified with PEI. On the other hand, little was reported on adsorption of metal ions on the membranes and beads prepared or modified with LPEI. Our objective in this study is focused on the preparation of a metal ion adsorptive membrane from a porous PE (pPE) film through the photografting of GMA and the subsequent functionalization by LPEI and BPEI, and the discussion of their adsorption and desorption properties and reusability. Here, the pPE film was used in the high specific surface area. An investigation was carried out on the adsorption properties of the LPEI- and BPEI-bonded (pPE-g-PGMA) (LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA)) films to  $\text{Cu}^{2+}$  ions as a function of the chemical structure of PEI (LPEI and BPEI), molecular mass of LPEI, amount of bonded PEI, pH value, and temperature. In addition, the reusability of the (LDPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films was also examined by alternatively repeating the cyclic process of adsorption and desorption.

## EXPERIMENTAL

### Materials

A porous polyethylene (pPE) film (thickness, 0.10  $\mu\text{m}$ ; pore size, 30  $\mu\text{m}$ , vacancy, 30%) purchased from Nitto Denko Co. (Osaka, Japan) was used as a polymer substrate. Glycidyl methacrylate (GMA) was purchased from Kishida Chemical Co. (Osaka, Japan) and used as received without further purification. BPEI ( $M_w$ : 7.0

$\times 10^4$ , concentration: 30%) was obtained from Wako Pure Chemical Co (Tokyo, Japan). PEOX samples with three different molecular mass such as PEOX no. 50 ( $M_w$ :  $5.0 \times 10^4$ ), PEOX no. 200 ( $M_w$ :  $2.0 \times 10^5$ ), and PEOX no. 500 ( $M_w$ :  $5.0 \times 10^5$ ) were supplied from Nihon Shokubai Co. (Tokyo, Japan). Other chemicals were used as received without further purification.

### Membrane preparation

#### Photografting of GMA on pPE films

The LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films were prepared by the photografting of GMA on the pPE films and the subsequent bonding of LPEI and BPEI chains on the pPE-g-PGMA films. The schematic representation of a sequence of the membrane preparation including the preparation of LPEI from poly(ethyloxazoline) (PEOX) was illustrated in Scheme 1. The experimental procedures were described in detail in the following.

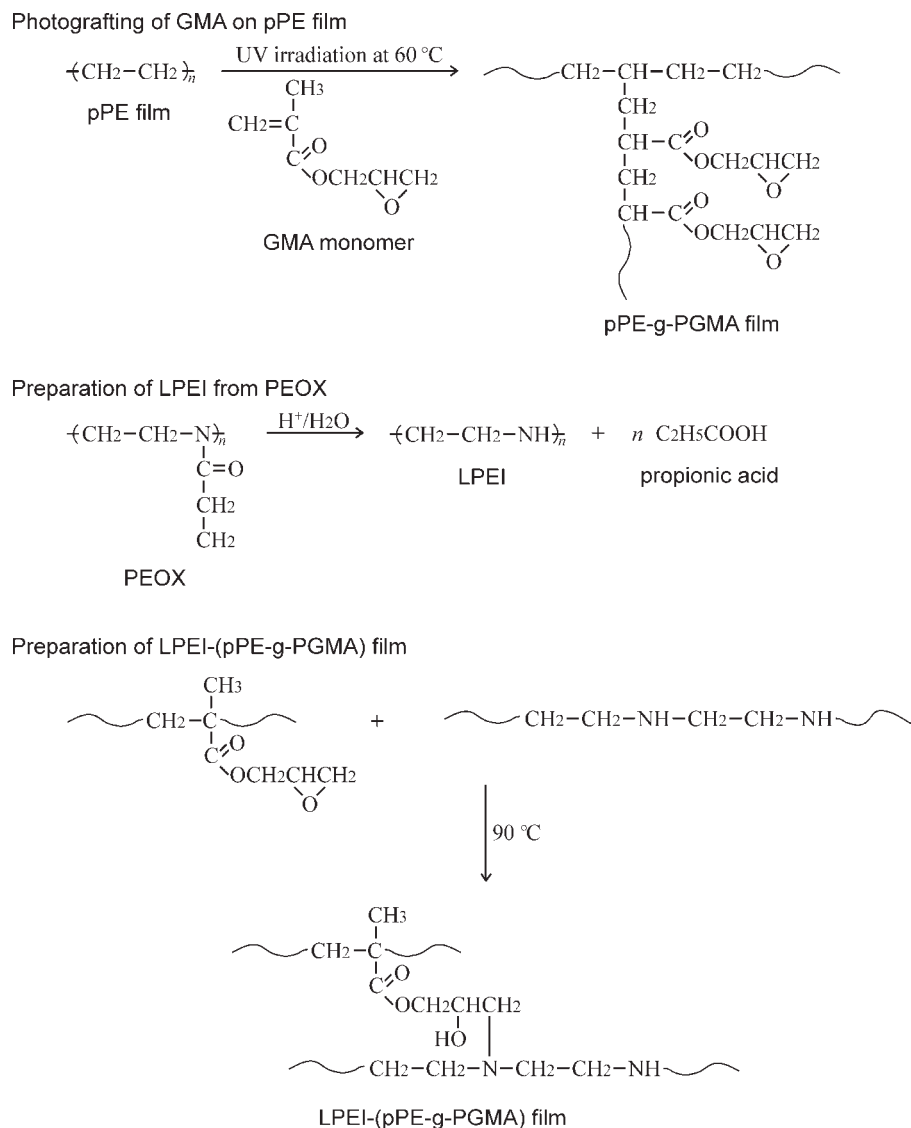
The pPE films cut into 6.0 cm in length and 3.0 cm in width were dipped for 1 min in an acetone solution containing benzophenone (BP) as a sensitizer (0.5 w/v %) to coat their surfaces with BP.<sup>4–10</sup> The photografting was carried out by applying UV rays emitted from a 400-W high-pressure mercury lamp. The BP-coated PE films were immersed in an aqueous 80 vol % ethanol solution of GMA monomer of 1.0M at 60°C in a Pyrex glass tube.<sup>22</sup> The amount of grafted GMA was calculated from the weight increase in mmol/g after photografting using eq. (1).

$$\begin{aligned}
 \text{Amount of grafted GMA (mmol/g)} \\
 = \frac{(W_g - W_0)/142.15}{W_0} \times 1000 \quad (1)
 \end{aligned}$$

where  $W_0$  and  $W_g$  denote the weight of the ungrafted pPE and pPE-g-PGMA films, respectively. The quantity of 142.15 is the molecular mass of GMA.

#### Bonding of BPEI and LPEI on pPE-g-PGMA films

LPEI was prepared by acid hydrolysis of PEOX as described below.<sup>26,27</sup> PEOX of 50 g was dissolved in water of 300  $\text{cm}^3$ . After conc. HCl of 76 g was added to the solution, the solution was refluxed for 24 h at 100–110°C. Subsequently, water of 200  $\text{cm}^3$  was added to the reaction solution, and then most of unreacted HCl and propionic acid as a byproduct were removed by eluting off the distillate of the same amount as water added. This procedure was repeated at least 10 times. Finally, when the solution was neutralized with 50% NaOH solution at 80°C, and then cooled to room temperature, crude white LPEI powders were precipitated. The LPEI powders were isolated by a G3 glass-filter and thoroughly washed with water and acetone. The purified LPEI powders were dried under reduced



**Scheme 1** Schematic representation of preparation of the PEI-(pPE-g-PGMA) films.

pressure. The structure of LPEI was identified in  $\text{CDCl}_3$  by  $^{13}\text{C}$  NMR. Only a sharp peak at 49.4 ppm assigned to carbon atoms in the LPEI backbone emerged. The density of amino groups was determined from the colloid titration measurements. The aqueous solutions of hydrochloride salt of LPEI, namely LPEI HCl ( $\sim 0.3 \text{ mg/cm}^3$ ), were titrated with an aqueous potassium poly(vinyl alcohol) sulfate (KPVS) solution (the concentration of sulfate groups =  $0.002503\text{M}$ ) adjusted to the pH values of the LPEI solutions using an ART-3 type HIRAMA automatic recording titrator.<sup>10,28,29</sup> The density of amino groups calculated from the end point determined by the turbidity at 420 nm was in fair agreement with the reciprocal of the molecular mass of the repeating unit of LPEI. Molecular mass of the LPEI samples prepared was calculated from molecular mass of PEOX officially published by the manufacturer and the repeat-

ing unit of LPEI. The LPEI samples prepared from PEOX no. 50, PEOX no. 200, and PEOX no. 500 were named 22K-LPEI ( $M_w = 2.2 \times 10^4$ ), 87K-LPEI ( $M_w = 8.7 \times 10^4$ ), and 220K-LPEI ( $M_w = 2.2 \times 10^5$ ), respectively.

The LPEI solutions in dimethyl sulfoxide (DMSO) and BPEI solutions in *N,N*-dimethylformamide (DMF) of 2 or 5% (w/v) were prepared. DMSO and DMF were selected as a solvent because the former was a good solvent for both LPEI and PGMA and the latter for both BPEI and PGMA, and both solvents had relatively high boiling points ( $189^\circ\text{C}$  for DMSO and  $153^\circ\text{C}$  for DMF). The pPE-g-PGMA films which beforehand swollen in DMSO or DMF were immersed in the LPEI or BPEI solutions, and then the reaction solutions were heated at  $90^\circ\text{C}$  with moderate stirring for 18 h. The amounts of bonded LPEI and BPEI were calculated in mmol/g from the weight increase after the

reaction and molecular mass of the repeating units of LPEI and BPEI (43.07 for LPEI and BPEI) using eq. (2).

$$\begin{aligned} \text{Amount of bonded PEI (mmol/g)} \\ = \frac{(W_{\text{PEI}} - W_g)/43.07}{W_g} \times 1000 \quad (2) \end{aligned}$$

where  $W_{\text{PEI}}$  denotes the weight of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films.

### Membrane properties of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films

The photografting of GMA on the pPE film and bonding of LPEI and BPEI on the pPE-g-PGMA films were confirmed on a Shimadzu ESCA-3400 type spectrometer with MgK $\alpha$  (1253.6 eV) source operating 8 kV and 20 mA.

Membrane properties of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films were investigated in the manner described in our previous articles.<sup>6,30</sup> The amount of absorbed water was calculated from the weight increase of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films immersed in distilled water for 24 h at 30°C. In addition, the  $n_{\text{water}}$  value, the number of bonded or assigned per LPEI or BPEI segment, was calculated from the amount of bonded PEI and the amount of absorbed water using eq. (3).

$$n_{\text{water}} = \frac{(W_W - W_{\text{PEI}})/18.016}{(W_{\text{PEI}} - W_g)/43.07} \quad (3)$$

where  $W_W$  denotes the weight of the LPEI-(pPE-g-PGMA) or BPEI-(pPE-g-PGMA) films swollen in water. In addition, the expansion of the pPE films by the bonding of PEI and water absorption was estimated from the area ratio. The original size of the pPE film was 18.0 cm<sup>2</sup> before photografting. The length and width were measured by a caliper, and the area ratios were calculated.

### Adsorption and desorption properties

The adsorption and desorption properties of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films to Cu<sup>2+</sup> ions were investigated in the manner described in our previous article.<sup>22</sup>

The LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films (4.0 × 4.0 cm<sup>2</sup>) swollen in the 0.05M HCl/NaCl (pH 1.0 and 2.0) or CH<sub>3</sub>COONa/CH<sub>3</sub>COOH (pH 3.0–5.0) buffers were placed in 50 cm<sup>3</sup> of CuCl<sub>2</sub> buffers (1.0 mM) of different pH values at 30°C, and then the solutions were mildly stirred. The amount of adsorbed Cu<sup>2+</sup> ions were spectrophotometrically determined

from Cu<sup>2+</sup> ion concentration of the surrounding solutions ( $\lambda = 207$  nm at pH 1.0 and 2.0 and  $\lambda = 242$  nm at pH 3.0–5.0). Desorption behavior was investigated by spectrophotometrically measuring the desorbed amount from the Cu<sup>2+</sup> ion-adsorbed LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films immersed in HCl solutions of different concentrations.

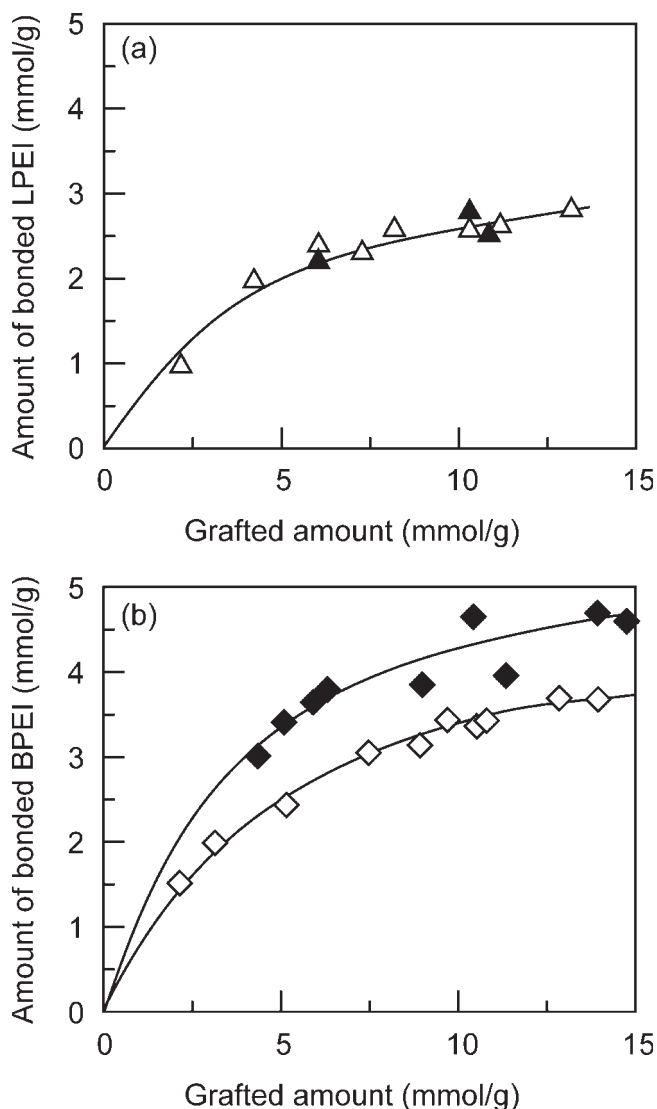
## RESULTS AND DISCUSSION

### Chelating functionalization and membrane properties

The photografting of GMA into the pPE films was carried out in an 1.0M GMA monomer solution at 60°C. The grafted amount increased with an increase in the irradiation time, and went up to 20 mmol/g at the irradiation time of 150 min. The grafted amount was adjusted by varying the irradiation time. A peak at 289 eV assigned to the carbon in carboxyl ester appeared in addition to a peak at 285 eV in the C1s spectra for the pPE-g-PGMA films. A relatively broad peak positioned at 532 eV was observed corresponding to the oxygen atoms in the carboxyl ester and terminal epoxy group in the O1s spectra.

In addition, the amount of bonded LPEI and BPEI was investigated as a function of the grafted amount, reaction time, and molecular mass of LPEI. The pPE-g-PGMA films were immersed in a DMSO solutions of LPEI and a DMF solution of BPEI, and then the solutions were heated at 90°C for 18 h. The amounts of bonded 87K-LPEI and BPEI increased with an increase in the grafted amount as shown in Figure 2. The bonding of LPEI and BPEI on the pPE-g-PGMA films takes place between an epoxy group appended to the grafted PGMA chains and a primary or secondary amino group appended to PEI. The bonding of LPEI and BPEI chains on grafted PGMA chains located in the inside of the grafted layer also occurs at higher grafted amounts. However, since the amount of bonded LPEI was independent of the LPEI concentration, the bonding of LPEI is considered to be more restricted to the vicinity of the surface region of the grafted layer than that of BPEI. Therefore, LPEI chains are more densely located in the grafted layer. This suggestion will be supported by the results of the water-absorptivity measurements described in the following.

Next, the effect of the reaction time on the amounts of the bonded LPEI and BPEI was investigated at the PEI concentration of 2 wt %. When either LPEI or BPEI chains were bonded to the pPE-g-PGMA films, a small N1s peak emerged at 399 nm. However, an O1s peak remained even at higher amounts of bonded PEI. This means that PEI chains are intermixed with grafted PGMA chains in the vicinity of the surface region of the grafted layer.



**Figure 2** Changes in the amount of bonded (a) 87K-LPEI and (b) BPEI with the grafted amount at 90°C. Conditions: (a) solvent: DMSO, reaction time: 18 h. (b) solvent: DMF, reaction time: 18 h. PEI concentration (wt %)-  $\triangle$ ,  $\diamond$ : 2,  $\blacktriangle$ ,  $\blacklozenge$ : 5.

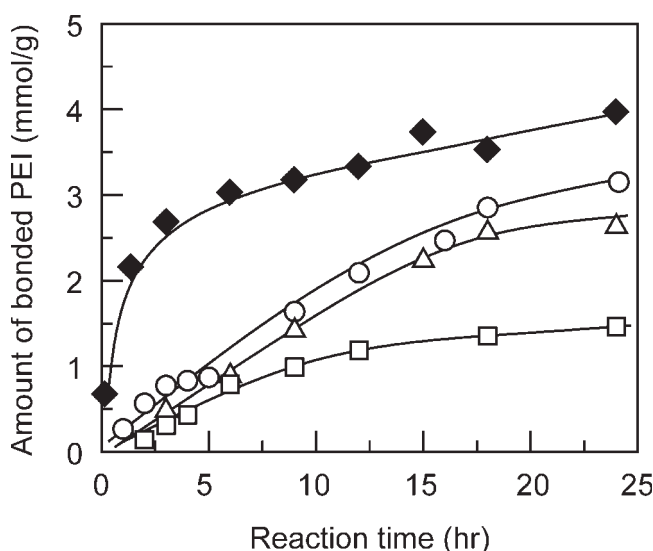
Figure 3 shows the changes in the amount of bonded PEI with the reaction time for the pPE-g-PGMA films of a constant grafted amount of about 10 mmol/g. The amount of bonded LPEI increased over the reaction time irrespective of molecular mass of LPEI used. However, the amount of bonded LPEI decreased with an increase in molecular mass of LPEI because the increase in molecular mass of LPEI was considered to constrict the penetration of LPEI chains into the grafted layers. A BPEI solution of 5 wt % was used to prepare the BPEI-(pPE-g-PGMA) films with higher bonded amounts. On the other hand, since the amount of bonded LPEI was little increased even by increasing the LPEI concentration of 2–5 wt % as shown in Figure 2(a), LPEI was bonded the resultant LPEI-(pPE-g-PGMA) films in a 2 wt % LPEI solution.

The pPE-g-PGMA films little swelled in water. The bonding of LPEI and BPEI confers the water-absorptivity to the pPE-g-PGMA films. Figure 4 shows the changes in the amount of absorbed water and the  $n_{\text{water}}$  value with the amount of bonded PEI for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films.

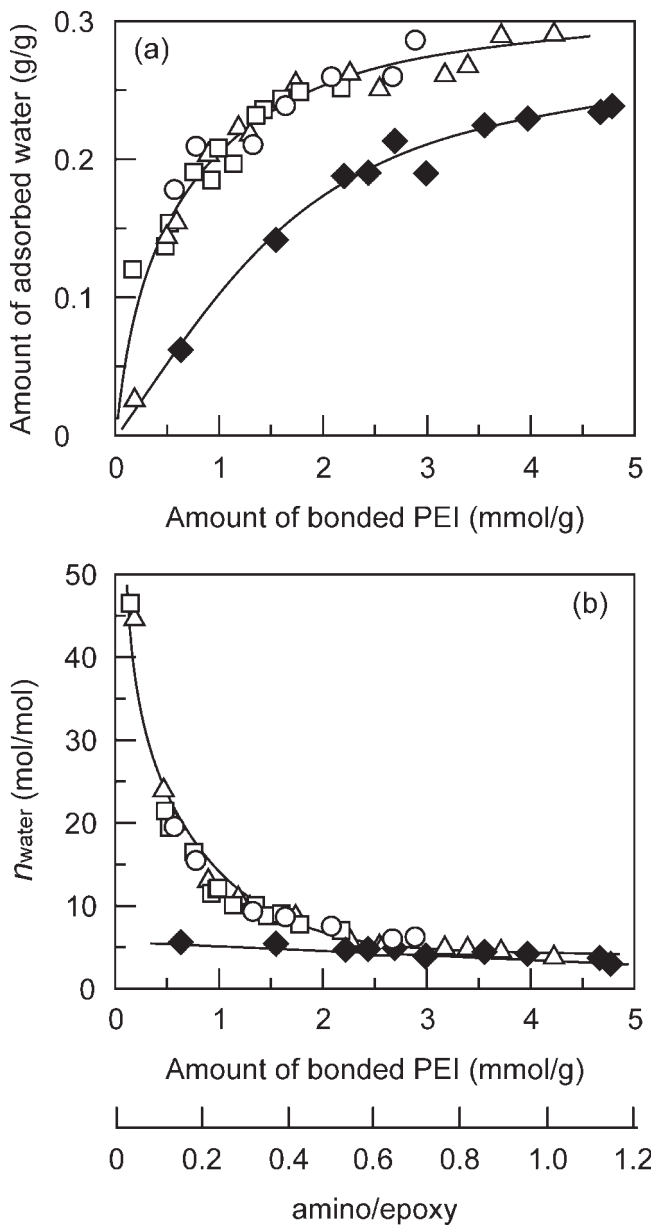
Here, since the grafted PGMA chains and bonded PEI chains in the grafted layer is considered to be not uniformly distributed throughout the grafted layer as described above, it is difficult to determine the density of amino groups in the grafted layer. Therefore, the ratio of the amount of primary, secondary, and tertiary amino groups of the bonded LPEI or BPEI chains to the epoxy groups appended to the grafted PGMA chains, the bonding ratio (amino/epoxy), was calculated as an alternative index of the density of amino groups in the grafted layer using eq. (4) and its scale was added to the  $x$  axis in the Figures 4 and 5.

$$\text{Bonding ratio} = \frac{(W_{\text{PEI}} - W_g)/43.07}{(W_g - W_0)/142.15} \quad (4)$$

The amount of absorbed water increased over the amount of bonded PEI and independent of molecular mass of LPEI for both PEI-(pPE-g-PGMA) films with a constant grafted amount. The water-absorptivity for the LPEI-(pPE-g-PGMA) films was higher than that for the BPEI-(pPE-g-PGMA) films. The  $n_{\text{water}}$  value for the LPEI-(pPE-g-PGMA) films sharply decreased against the amount of bonded LPEI. This will be caused by bonding of LPEI on grafted PGMA chains present the inside of the grafted layer and/or crowding of bonded LPEI chains in the grafted layers at



**Figure 3** Changes in the amounts of bonded LPEI (open) and BPEI (shaded) with the reaction time for the pPE-g-PGMA films of the grafted amount of 10.2 mmol/g. PEI concentration: 2 wt %. PEI sample-  $\circ$ : 22K-LPEI,  $\triangle$ : 87K-LPEI,  $\square$ : 220K-LPEI,  $\blacklozenge$ : BPEI.

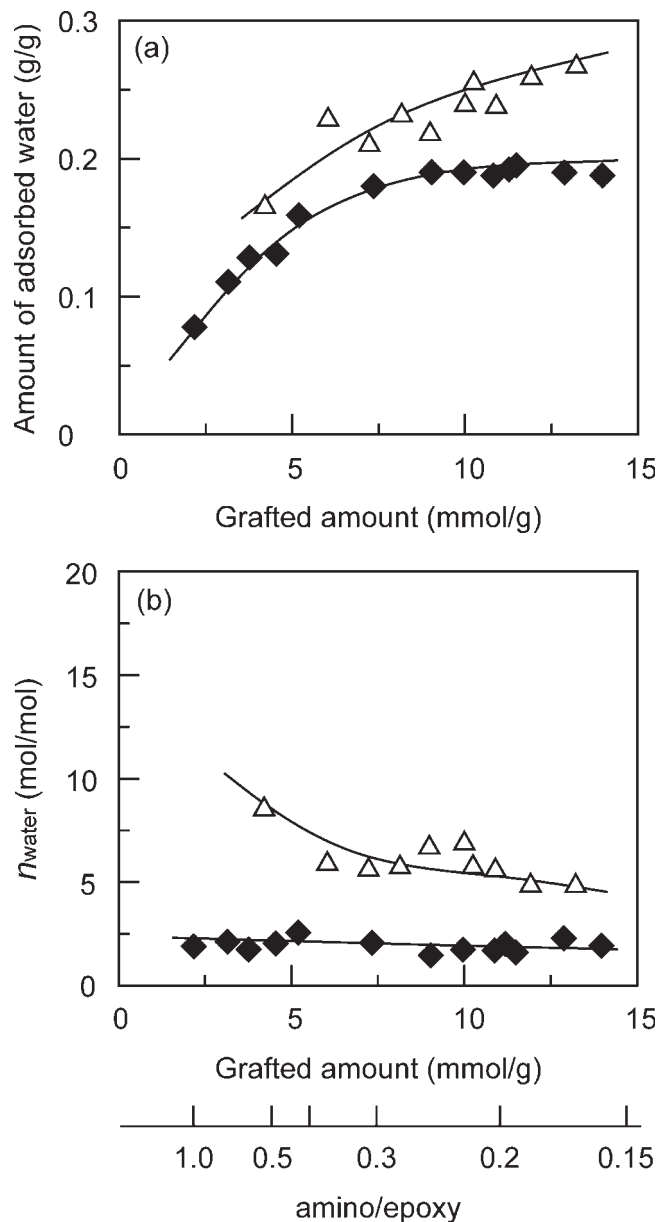


**Figure 4** Changes in the (a) amount of adsorbed water and (b)  $n_{\text{water}}$  value with the amount of bonded PEI for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films of the grafted amount of 10.2 mmol/g at 30°C. PEI sample: ○: 22K-LPEI, △: 87K-LPEI, □: 220K-LPEI, ◆: BPEI.

higher grafted amounts. Therefore, the amount of adsorbed water is considered to tend to level off at higher grafted amounts. The  $n_{\text{water}}$  value for the BPEI-(pPE-g-PGMA) films was much lower than that for the LPEI-(pPE-g-PGMA) films because of bulkiness of the BPEI chains and gradually decreased with an increase in the amount of bonded BPEI. The presence of tertiary amino groups and their additional formation would result in the decrease in the water-absorptivity for the BPEI-(pPE-g-PGMA) films. It was found from these results that the LPEI-(pPE-g-PGMA) films

had higher water-absorptivity than the BPEI-(pPE-g-PGMA) films irrespective of molecular mass of LPEI bonded.

A constant amount of 87K-LPEI or BPEI (2.1 mmol/g for LPEI and 2.2 mmol/g for BPEI) was bonded to the pPE-g-PGMA films with different grafted amounts. Figure 5 shows the changes in the amount of adsorbed water and the  $n_{\text{water}}$  value with the grafted amount for the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with a constant amount of bonded LPEI or BPEI. The amount of adsorbed water sharply in-



**Figure 5** Changes in the (a) amount of adsorbed water and (b)  $n_{\text{water}}$  value with the grafted amount for the 87K-LPEI-(pPE-g-PGMA) (△, the amount of bonded 87K-LPEI = 2.1 mmol/g) and BPEI-(pPE-g-PGMA) (◆, the amount of bonded BPEI = 2.2 mmol/g) films.

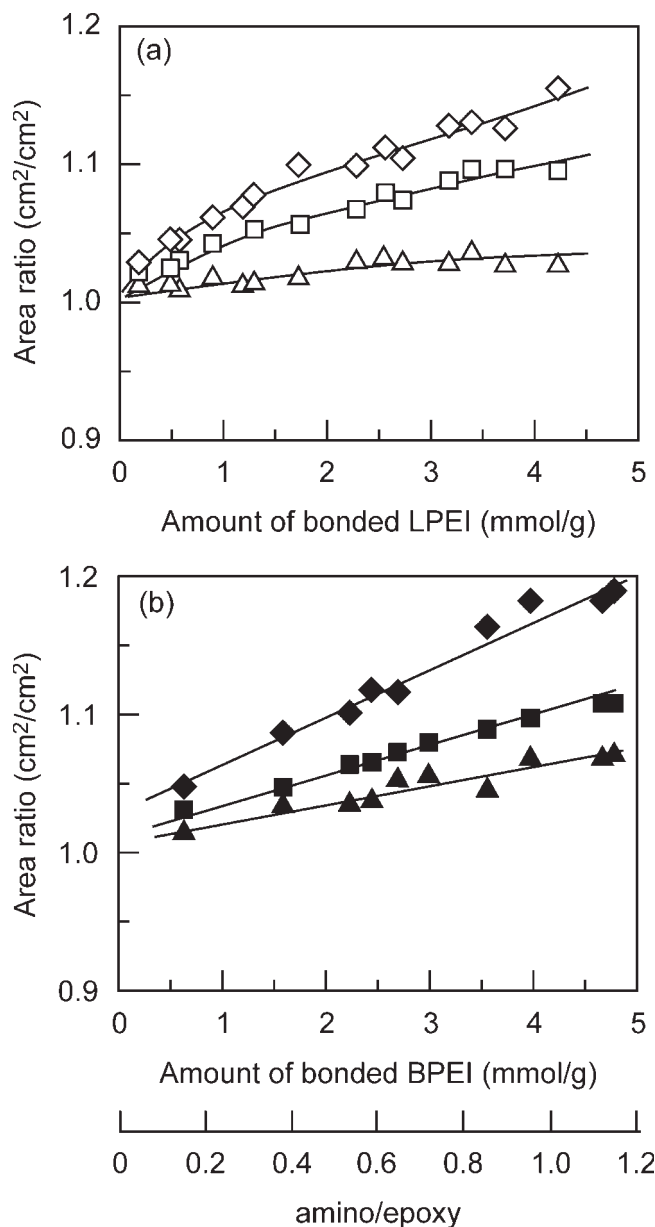
creased with an increase in the grafted amount at lower grafted amounts. However, when the grafted amount exceeded about 10 mmol/g, the amount of absorbed water tended to level off. Contrary to this, the  $n_{\text{water}}$  value decreased over the grafted amount. Since some of the PEI chains also bond to grafted PGMA chains located in the inside of the grafted layer at higher grafted amounts, the density of bonded PEI chains in the grafted layer is considered to decrease with an increase in the grafted amount. In other words, the amounts of bonded 87K-LPEI and BPEI were too low to make the pPE-g-PGMA films adequately hydrophilic at higher grafted amounts. The increase in the water-absorptivity at lower grafted amounts is due to hydrophilization caused by bonding of LPEI and BPEI chains as the typical water-soluble cationic polyelectrolyte. The fact that the  $n_{\text{water}}$  value gradually decreased with an increase in the grafted amount will support our consideration on bonding LPEI and BPEI described above.

The expansion of the pPE films by both bonding of PEI chains and water adsorption was estimated from the area ratio. Figure 6 shows the dimensional change by bonding of PEI and water adsorption for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with a constant grafted amount of 10.2 mmol/g. The pPE films were expanded by the photografting of GMA like the nonporous PE films photografted with methacrylic acid, AA, 2-(dimethylamino)ethyl methacrylate, *N*-isopropylacrylamide, and GMA.<sup>4-6,9</sup> The subsequent bonding of LPEI and BPEI caused the pPE-g-PGMA films to expand. In addition, the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films more expanded by water adsorption. The area ratio of the BPEI-(pPE-g-PGMA) films was a little higher than that of the LPEI-(pPE-g-PGMA) films in the water-swollen state, although the definite difference in the expansion by the bonding of LPEI and BPEI wasn't observed. This result supports our suggestion that the bonding of LPEI is more restricted to the vicinity of the surface region of the grafted layer than that of BPEI.

#### $\text{Cu}^{2+}$ ion adsorption properties of LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films

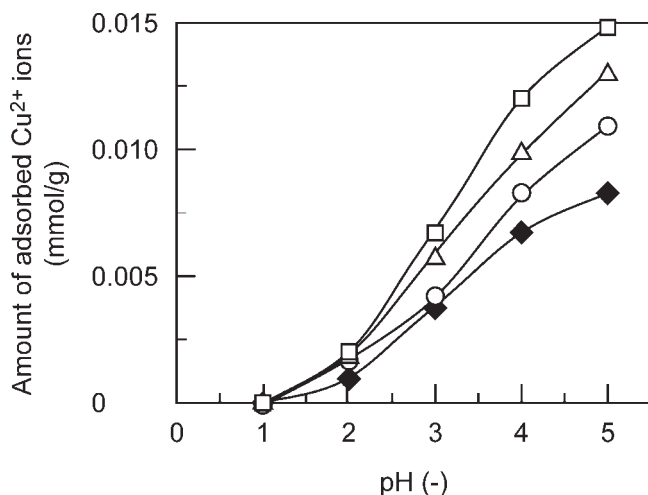
The effect of the pH value

The LPEI-(pPE-g-PGMA) films with the grafted amount of 10.2 mmol/g and the bonded amount of 2.2 mmol/g and a BPEI-(pPE-g-PGMA) film with the grafted amount of 9.8 mmol/g and the bonded amount of 2.2 mmol/g were immersed in the  $\text{CuCl}_2$  solutions of pH 1.0–5.0 at 30°C. Figure 7 shows the pH dependence on the  $\text{Cu}^{2+}$  ion adsorption for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. The amount of adsorbed  $\text{Cu}^{2+}$  ions increased with an increase in the pH value and had the maximum value



**Figure 6** Changes in the area ratio with the amount of bonded PEI for the (a) 87K-LPEI-(pPE-g-PGMA) (open) and (b) BPEI-(pPE-g-PGMA) (shaded) films of the grafted amount of 10.2 mmol/g. Area ratio (cm<sup>2</sup>/cm<sup>2</sup>)-  $\Delta$ : water-swollen PEI-(pPE-g-PGMA)/dry PEI-(pPE-g-PGMA),  $\square$ : dry PEI-(pPE-g-PGMA)/dry pPE-g-PGMA,  $\diamond$ : water-swollen PEI-(pPE-g-PGMA)/dry pPE-g-PGMA.

at pH 5.0. The amount of adsorbed  $\text{Cu}^{2+}$  ions for the LPEI-(pPE-g-PGMA) film was higher than that for the BPEI-(pPE-g-PGMA) film irrespective of molecular mass of the LPEI used. Some of the secondary amino groups were converted into the tertiary amino groups by bonding of BPEI chains to a grafted PGMA chain. Since a LPEI chain has only secondary amino groups, tertiary amino groups were formed only by the bonding of the LPEI chains to the grafted PGMA chains. The quantities of amino groups of 25% were tertiary



**Figure 7** Changes in the amount of adsorbed  $\text{Cu}^{2+}$  ions with the pH value for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films of the amount of bonded PEI of 2.2 mmol/g at  $30^\circ\text{C}$  in the initial  $\text{CuCl}_2$  concentration of 1.0 mM. The grafted amount: 10.2 mmol/g for the LPEI-(pPE-g-PGMA) films and 9.8 mmol/g for the BPEI-(pPE-g-PGMA) films. PEI sample-  $\circ$ : 22K-LPEI,  $\triangle$ : 87K-LPEI,  $\square$ : 220K-LPEI,  $\blacklozenge$ : BPEI.

amino groups for BPEI and the net amount of tertiary amino groups increased by bonding on grafted PGMA chains. The low  $\text{Cu}^{2+}$  ion adsorption for the BPEI-(pPE-g-PGMA) films was considered to be due to higher density of tertiary amino groups.

The idealized structure of the polymeric complex between a LPEI chain and Cu ions is shown by Molinari et al., where the lone-pair of nitrogen binds  $\text{Cu}^{2+}$  ions according to the acid and base Lewis theory.<sup>31</sup> A Cu ion binds a LPEI chain through the complexation of a  $\text{Cu}^{2+}$  ion with four nitrogen atoms on the LPEI chain. The presence of tertiary amino groups is considered to have an adverse effect to adsorption of  $\text{Cu}^{2+}$  ions. In addition, the increase in molecular mass of LPEI led to the increase in the amount of adsorbed  $\text{Cu}^{2+}$  ions because LPEI chains with higher molecular mass are considered to have higher mobility in a buffer even after bonding. At pH 5.0, the amount of adsorbed  $\text{Cu}^{2+}$  ions for the 220K-LPEI-(pPE-g-PGMA) film was 1.5 times as high as that for the 22K-LPEI-(pPE-g-PGMA) film. This indicates the increase in the molecular mass of the LPEI chains bonded has a favorable influence on the adsorption of  $\text{Cu}^{2+}$  ions.

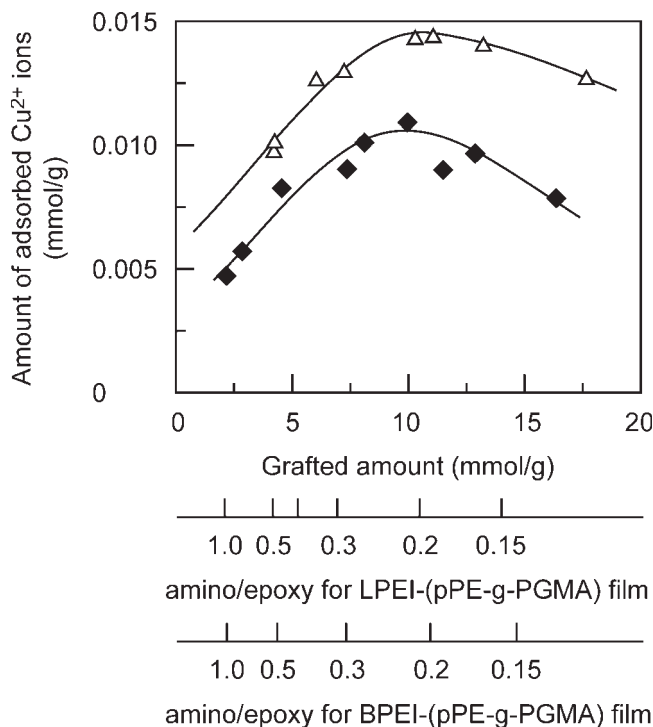
#### The effect of the grafted amount

The LPEI and BPEI chains were bonded to pPE-g-PGMA films with different grafted amounts in such a way that the pPE-g-PGMA films had a constant amount of bonded LPEI and BPEI (2.1 mmol/g for the LPEI-(pPE-g-PGMA) films and 2.2 mmol/g for the BPEI-(pPE-g-PGMA) films). Figure 8 shows the variations in the amount of  $\text{Cu}^{2+}$  ions with the grafted

amount for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with a constant bonded amount at pH 5.0 and  $30^\circ\text{C}$ . The amount of adsorbed  $\text{Cu}^{2+}$  ions went through the maximum value at the grafted amount of 10 mmol/g. The LPEI and BPEI chains bonded are more densely located in the grafted layers at lower grafted amounts. When the grafted amount exceeded 10 mmol/g, LPEI and BPEI chains would also bond to the grafted PGMA chains present in the inside of the grafted layer. From the result shown in Figure 8, the effect of the amount of bonded PEI and temperature on  $\text{Cu}^{2+}$  ion adsorption was investigated at pH 5.0 for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with the grafted amount of 10.1 mmol/g.

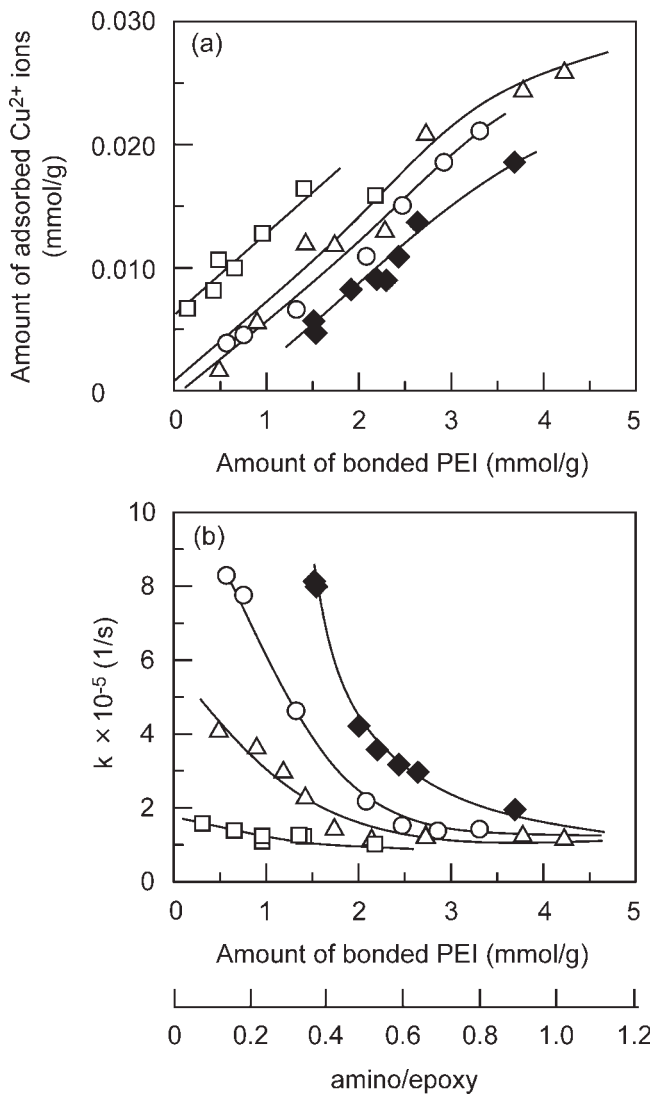
#### The effect of the amount of bonded PEI

The  $\text{Cu}^{2+}$  ion adsorptivity was estimated in an 1.0 mM  $\text{CuCl}_2$  buffer at pH 5.0 and  $30^\circ\text{C}$  for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films of the grafted amount of 10.1 mmol/g with different bonded amounts of PEI. Figure 9 shows the changes in the amount of adsorbed  $\text{Cu}^{2+}$  ions and the kinetic constant of adsorption with the amount of bonded PEI at pH 5.0 and  $30^\circ\text{C}$ . The amount of adsorbed  $\text{Cu}^{2+}$  ions increased with an increase in the amount of bonded



**Figure 8** Changes in the amount of adsorbed  $\text{Cu}^{2+}$  ions with the grafted amount for the 87K-LPEI-(pPE-g-PGMA) ( $\triangle$ ) and BPEI-(pPE-g-PGMA) ( $\blacklozenge$ ) films of a average amount of bonded PEI (2.1 mmol/g for the LPEI-(pPE-g-PGMA) films and 2.2 mmol/g for the BPEI-(pPE-g-PGMA) films) at pH 5.0 and  $30^\circ\text{C}$  in the initial  $\text{CuCl}_2$  concentration of 1.0 mM.





**Figure 9** Changes in the (a) amount of adsorbed  $\text{Cu}^{2+}$  ions and (b) value of kinetic constant of adsorption with the amount of bonded PEI for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films of the grafted amount of 10.1 mmol/g at pH 5.0 and 30°C in the initial  $\text{CuCl}_2$  concentration of 1.0 mM. PEI sample- ○: 22K-LPEI, △: 87K-LPEI, □: 220K-LPEI, ◆: BPEI.

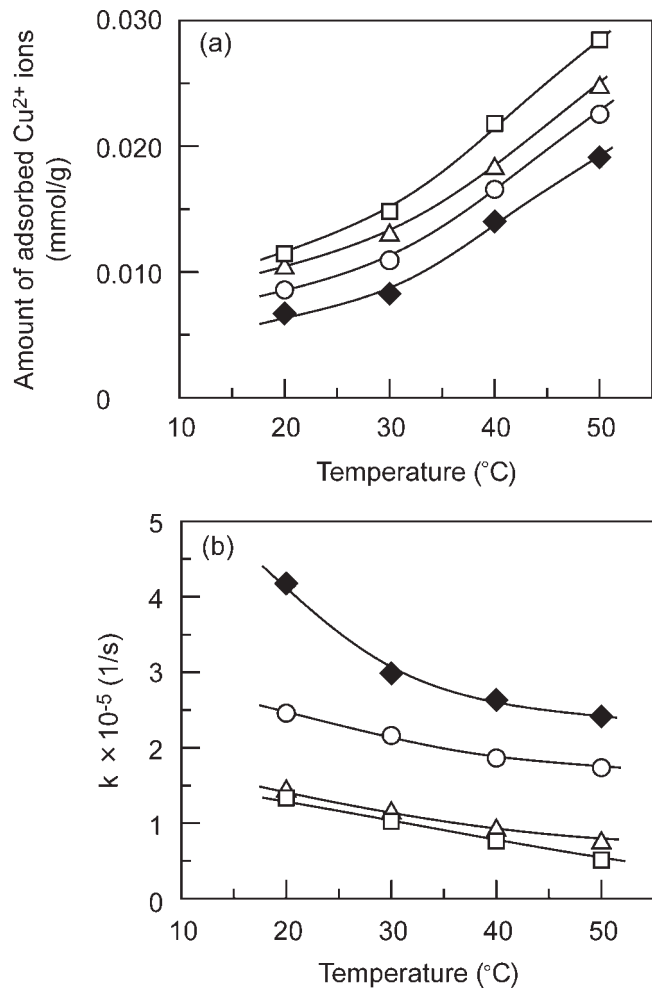
PEI and the LPEI-(pPE-g-PGMA) films had higher adsorptivity to  $\text{Cu}^{2+}$  ions than the BPEI-(pPE-g-PGMA) films. In addition, the  $\text{Cu}^{2+}$  ion adsorptivity for the LPEI-(pPE-g-PGMA) films increased with an increase in molecular mass of LPEI. However, the value of kinetic constant of adsorption decreased with an increase in molecular mass of LPEI as shown in Figure 9(b). The value of kinetic constant of adsorption for the BPEI-(pPE-g-PGMA) films significantly decreased in the range of the grafted amounts lower than 3.0 mmol/g. The main reason is explained as follows.  $\text{Cu}^{2+}$  ions are also adsorbed on the LPEI and BPEI chains bond to the grafted PGMA chains present in the inside of the grafted layer. In addition, as the

amount of bonded LPEI and BPEI increased, it took longer times to reach the adsorption equilibrium.

#### The effect of temperature

The temperature dependence of  $\text{Cu}^{2+}$  ion adsorption was investigated in a 1.0 mM  $\text{CuCl}_2$  solution of pH 5.0. Figure 10 shows the temperature dependence of  $\text{Cu}^{2+}$  ion adsorption for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films.

The amount of adsorbed  $\text{Cu}^{2+}$  ions increased and the value of kinetic constant of adsorption decreased with an increase in the temperature. The increase in the temperature led to the increase in the capture of  $\text{Cu}^{2+}$  ions with LPEI and BPEI chains. However, since the increase in the amount of adsorbed  $\text{Cu}^{2+}$  ions was caused by the adsorption of  $\text{Cu}^{2+}$  ions on the LPEI



**Figure 10** Changes in the (a) amount of adsorbed  $\text{Cu}^{2+}$  ions and (b) value of kinetic constant of adsorption with the temperature for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with the grafted amount of 10.1 mmol/g and the amount of bonded PEI of 2.2 mmol/g at pH 5.0 and 30°C in the initial  $\text{CuCl}_2$  concentration of 1.0 mM. PEI sample- ○: 22K-LPEI, △: 87K-LPEI, □: 220K-LPEI, ◆: BPEI.

and BPEI chains bonded to the grafted PGMA chains located in the inside of the grafted layer, it took longer times to reach the adsorption equilibrium. In addition, the value of kinetic constant of adsorption decreased with an increase in molecular mass of LPEI. Therefore, the value of kinetic constant of adsorption is considered to decrease over the temperature. However, the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films would be susceptible to deterioration and fatigue at higher temperatures.

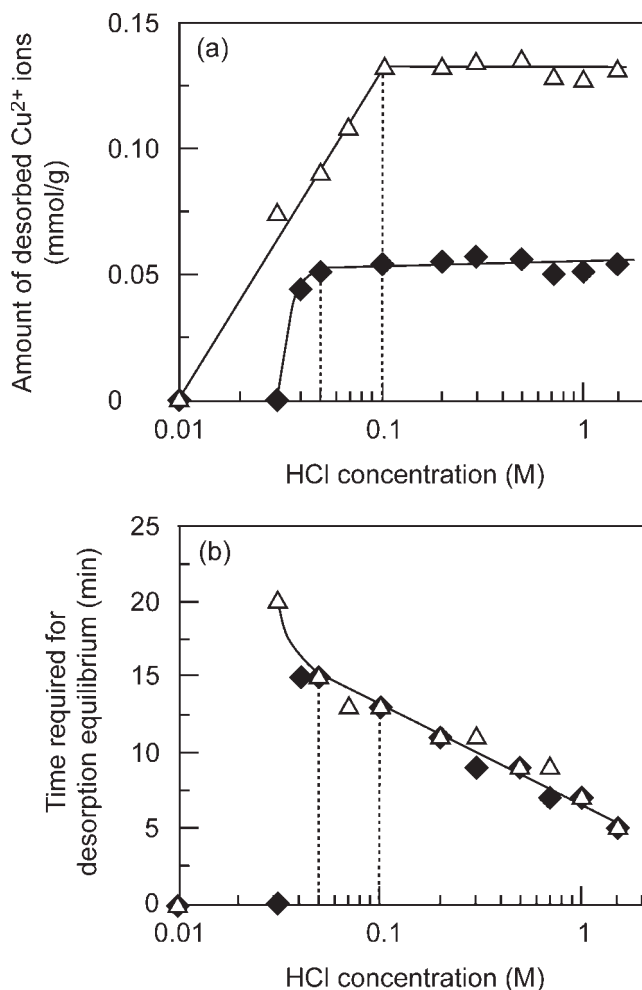
### Dependence of $\text{Cu}^{2+}$ ion desorption on HCl concentration

The effect of HCl concentration on desorption of  $\text{Cu}^{2+}$  ions was investigated by immersing the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films which had reached the equilibrium adsorption, in the aqueous HCl solutions of 0.01–1.0M at 30°C. The amount of  $\text{Cu}^{2+}$  ions desorbed from the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films increased with an increase in the immersion time, and then leveled off irrespective of the HCl concentration. Figure 11 shows the changes in the amount of desorbed  $\text{Cu}^{2+}$  ions and the time required to reach the desorption equilibrium with the HCl concentration.  $\text{Cu}^{2+}$  ions were desorbed in the HCl solutions of more than 0.025M for an 87K-LPEI-(pPE-g-PGMA) film and more than 0.04M for a BPEI-(pPE-g-PGMA) film. The amount of desorbed  $\text{Cu}^{2+}$  ions increased with an increase in the HCl concentration for both PEI-(pPE-g-PGMA) films. The time required to reach the equilibrium desorption was shortened with an increase in the HCl concentration. The majority of  $\text{Cu}^{2+}$  ions were desorbed in the HCl solutions of more than 0.1M for the 87K-LPEI-(pPE-g-PGMA) film and of more than 0.05M for the BPEI-(pPE-g-PGMA) film.

There are many reports on adsorption of metal ions on various chelating membranes and beads,<sup>12–26</sup> and little on desorption of metal ions in acidic solutions of different concentrations.<sup>21,23,24,26</sup> The minimum HCl concentration to desorb the  $\text{Cu}^{2+}$  ions from the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films prepared in this study was much lower than those from metal ion adsorptive chelating membranes and beads prepared in other related studies.<sup>26</sup> Desorption of  $\text{Cu}^{2+}$  ions at lower HCl concentrations will constrict deterioration and fatigue of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films.

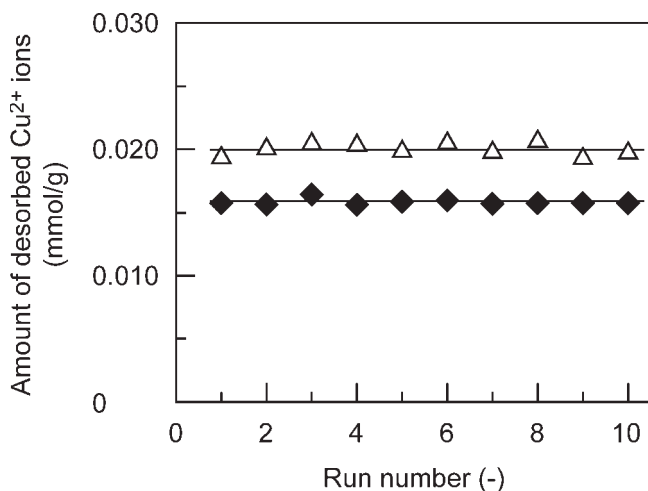
### Repetitive $\text{Cu}^{2+}$ ion adsorption

On the basis of the results on the pH dependence of adsorption of  $\text{Cu}^{2+}$  ions as shown in Figure 6 and the HCl concentration dependence of their desorption as shown in Figure 11, the cyclic process of adsorption at pH 5.0 and desorption in an HCl solution was alter-



**Figure 11** Changes in (a) the amount of desorbed  $\text{Cu}^{2+}$  ions and (b) the time required for desorption equilibrium with the HCl concentration for the 87K-LPEI-(pPE-g-PGMA) ( $\Delta$ ) and BPEI-(pPE-g-PGMA) ( $\blacklozenge$ ) films with the grafted amount of 9.9 mmol/g and the amount of bonded PEI of 3.2 mmol/g at 30°C.

nately repeated for the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. The concentration of HCl solution was adjusted to 0.1 and 0.05M for the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films, respectively. Figure 12 shows 10 successive  $\text{Cu}^{2+}$  ion adsorption processes for the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. When the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films were put back in a  $\text{CuCl}_2$  solution at pH 5.0 after each adsorption process,  $\text{Cu}^{2+}$  ions were adsorbed on the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. The amount of  $\text{Cu}^{2+}$  ions was almost equivalent in each adsorption process. The constant amount of adsorbed  $\text{Cu}^{2+}$  ions in each adsorption process indicates that when the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films were immersed in the HCl solutions after each  $\text{Cu}^{2+}$  adsorption, the majority of  $\text{Cu}^{2+}$  ions adsorbed were desorbed from the 87K-



**Figure 12** The repeated process of adsorption in a 1.0 mM CuCl<sub>2</sub> solution at pH 5.0 for the 87K-LPEI-(pPE-g-PGMA) (△) and BPEI-(pPE-g-PGMA) (◆) films with the grafted amount of 9.9 mmol/g and the amount of bonded PEI of 3.2 mmol/g at 30°C. Desorption was carried out in an aqueous 0.1M HCl solution at 30°C after each Cu<sup>2+</sup> ion adsorption.

LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. Therefore, it can be said that no isolation of LPEI and BPEI takes place during the adsorption and desorption experiments. These results indicate that the 87K-LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films are practically acid-proof and can endure several cycles of adsorption and desorption experiments without considerable fatigue.

## CONCLUSIONS

We have investigated the adsorption and desorption properties of the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films to Cu<sup>2+</sup> ions and their repetitive adsorption processes. From the experimental results above, we can conclude the following:

The amount of LPEI and BPEI bonded to the pPE-g-PGMA films increased over the reaction time. As the LPEI chains became shorter, the amount of bonded LPEI more sharply increased against the reaction time. The bonding of the LPEI and BPEI chains had the pPE-g-PGMA films more hydrophilic, and the amount of absorbed water increased with an increase in the amount of bonded PEI for both LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films. The amount of adsorbed Cu<sup>2+</sup> ions increased with an increase in the pH value in the range of 1.0–5.0 and had the maximum value at the grafted amount of 10 mmol/g for the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films with a constant amount of bonded PEI. The LPEI-(pPE-g-PGMA) films had higher adsorptivity to Cu<sup>2+</sup> ions than the BPEI-(pPE-g-PGMA) films and the

increase in molecular mass of LPEI led to the increase in the amount of adsorbed Cu<sup>2+</sup> ions. The amount of Cu<sup>2+</sup> ions desorbed from the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films increased with an increase in the concentration of HCl and the majority of Cu<sup>2+</sup> ions were desorbed in the HCl concentrations higher than 0.1M for the LPEI-(pPE-g-PGMA) films and higher than 0.05M for the BPEI-(pPE-g-PGMA) films. The time required to reach the desorption equilibrium became shorter with an increase in the HCl concentration. When adsorption of Cu<sup>2+</sup> ions at pH 5.0 and desorption in an aqueous HCl solution were repeatedly carried out, the amount of adsorbed Cu<sup>2+</sup> ions was almost constant at each adsorption experiment. This indicates that the majority of Cu<sup>2+</sup> ions are desorbed in the aqueous HCl solutions after each adsorption experiments, and the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films undergo little deterioration and fatigue during repeated adsorption and desorption experiments. It is made clear from the above results that the LPEI-(pPE-g-PGMA) and BPEI-(pPE-g-PGMA) films are used as a repeatedly generative membrane for metal ion adsorption.

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