Adsorption and Desorption Properties of the Chelating Membranes Prepared from the PE films

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ABSTRACT: The chelating membranes for adsorption of metal ions were prepared by the photografting of glycidyl methacrylate (GMA) onto a polyethylene (PE) film and the subsequent modification of the resultant GMA-grafted PE (PE-g-PGMA) films with disodium iminodiacetate in an aqueous solution of 55% DMSO at 80°C. The adsorption and desorption properties of the iminodiacetate (IDA) group-appended PE-g-PGMA (IDA-(PE-g-PGMA)) films to Cu^{2+} ions were investigated as functions of the grafted amount, pH value, Cu^{2+} ion concentration, and temperature. The amount of adsorbed Cu^{2+} ions increased with an increase in the pH value in the range of 1.0–5.0. The time required to reach the equilibrium adsorption decreased with an increase in the temperature, although the degree of adsorption stayed almost constant. The amount of Cu^{2+} ions desorbed from the (IDA-(PE-g-PGMA)) films increased and the time required to reach the equilibrium desorption decreased with an increase in the HCl concentration. About 100% of Cu^{2+} ions were desorbed in the aqueous HCl solutions of more than 0.5M. The amounts of adsorbed and desorbed Cu^{2+} ions were almost the same in each cyclic process of adsorption in a $CuCl_2$ buffer at pH 5.0 and desorption in an aqueous 1.0M HCl solution. These results indicate that the IDA-(PE-g-PGMA) films can be applied to a repeatedly generative chelating membrane for adsorption and desorption of metal ions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1895–1902, 2006

Key words: photografting; polyethylene; chelating membrane; adsorption; desorption

INTRODUCTION

Membrane technology is now targeting the development of novel membranes with various functionalities. The introduction of an ion-exchange group or an affinity ligand to insoluble support materials enables us to remove various undesirable ions from wastewater.[1] Although many polymer membranes and hydrogels have been prepared for different purposes, the mechanical properties of most of them are not necessarily adequate for them to act as functional membranes in the water-swollen state. We have prepared functional membranes from widely used polymer materials such as polyethylene (PE)[2–6] or expanded and porous poly(tetrafluoroethylene) (ePTFE and pPTFE)[7,8] films by the photografting of ionic, functional, or reactive monomers such as methacrylic acid (MAA),[7] acrylic acid (AA),[5] 2-(dimethylamino)ethyl methacrylate (DMAEMA),[2–4,7,8] isopropylacrylamide (NIPAAm),[2] methacrylamide (MAAm),[6] and glycidyl methacrylate (GMA).[6]

The grafting technique is one of the most outstanding procedures to chemically modify the polymer materials. The initiation of grafting includes [60]Co γ-ray irradiation, UV irradiation, plasma treatment, and so on. Of these, the radiation-induced grafting technique with UV[9–12] or [60]Co γ-ray[13–15] and subsequent functionalization[16–18] are mainly applied to modify the polyolefins such as PE and polypropylene because these techniques make it easy to control the initial site for the photografting and the density of the functional groups.[2,4,6,8] Therefore, we have applied the photografting technique with UV rays for the preparation of functional membranes from the PE films.

Since one end of a grafted polymer chain is covalently bonded to the surface of the polymer substrate and the other end is not put under restraint, the grafted polymer chains in the grafted layers show a high mobility in a good solvent. In addition, various functional groups consecutively affixed to the grafted polymer chains work as a fixed carrier. For more than one decade, our work has been geared toward studying the application of the grafted PE, pPTFE, and ePTFE films as functional membranes for permeation control,[2] separation,[3] concentration,[3,19] and adsorption of various ionic compounds in response to the temperature,[2] pH value,[2,3] and electrical field.[4,19] Recently, the necessity for heavy metal ion recovery processes in industrial and environmental applications

and the subsequent reuse of them have led to an increasing interest in selective ion exchange.[20–26]

Our objective in this study is to prepare chelate-forming membranes from a low-density PE (LDPE) film through the photografting and subsequent functionalization, and to assess their adsorption and desorption properties and reusability. Separation techniques using a chelating membrane are applicable mainly to the removal of metal ions through the capture of metal ions by chelate-forming functional groups affixed to the grafted polymer chains. In addition, a membrane system has become a practical alternative to the bead system conventionally used for adsorption and separation in facile handling. Many researchers have reported on the adsorption of various metal ions on the chelating membranes,[16–18] fibers,[27] and beads or resins.[20–26] However, little was reported on the dependence of metal ion adsorption on chelating-functional group density, pH value, and temperature and the cyclic adsorption–desorption process for their reuse.[25,28,29] In many studies, reactive monomers such as AA,[17] GMA,[21–23] and styrene[20,24] were copolymerized with hydrophobic monomers in the presence of a bifunctional crosslinker to prepare water-insoluble membranes and beads, and then the chelate-forming functional groups were introduced to the resultant membranes and beads. On the other hand, we aimed at preparing the practically reusable chelating membranes from the generally used polymers.

In this study, a reactive monomer, GMA, was photografted into the LDPE films. The chelating membranes with iminodiacetate (IDA) groups were prepared through a simple one-step reaction with disodium iminodiacetate (IDA2Na) from the GMA-grafted PE (PE-g-PGMA) films. An investigation was carried out on the adsorption properties of the IDA group-appended PE-g-PGMA (IDA-(PE-g-PGMA)) films to Cu^{2+} ions as a function of the amount of grafted GMA, pH value, Cu^{2+} ion concentration, and temperature. In addition, the reusability of the IDA-(PE-g-PGMA) films was also examined by alternatively repeating the cyclic process of adsorption and desorption.

EXPERIMENTAL

Photografting and chelating functionalization

A LDPE film (thickness, 30 μm; density, 0.924 g/cm^3) supplied from Tamapoly Co. Ltd., (Japan) was used as a polymer substrate for the photografting. The photografting of GMA into the PE films was carried out as described in our earlier papers.[2,3,4,6,19] The PE films cut into 6.0 cm length and 3.0 cm 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. 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 using a Pyrex glass tube. The amount of grafted GMA was calculated from the increase in weight in mmol/g-PE after photografting.

The PE-g-PGMA films were immersed in the aqueous DMSO solutions of different volume fractions of DMSO containing IDA2Na of 0.425M, and then the reaction solutions were heated at 80°C with moderate stirring for 24 h. The conversion from epoxy to IDA groups was calculated from the weight increase after the chelating reaction.[18,30,31]

Adsorption and desorption properties

The IDA-(PE-g-PGMA) films (10 $\times$ 10 mm^2) swollen in the 0.05M HCl/NaCl (pH 1.0 and 2.0) or acetate (pH 3.0–5.0) buffers (0.01 H) were placed in 100 cm^3 of CuCl$_2$ buffers (1.0 mM) of different pH values at 30°C, and then the solutions were mildly stirred. The amount of adsorbed Cu^{2+} ions was spectrophotometrically determined from Cu^{2+} ion concentration of the surrounding solutions (λ = 207 nm at the pH values of 1.0 and 2.0, and λ = 242 nm at the pH values of 3.0–5.0). Desorption behavior was investigated by spectrophotometrically measuring the desorbed amount from the Cu^{2+} ion-adsorbed IDA-(PE-g-PGMA) films immersed in the HCl solutions of different concentrations.

RESULTS AND DISCUSSION

### Chelating functionalization and membrane properties

PE-g-PGMA films of different grafted amounts were prepared by varying the UV-ray irradiation time in an aqueous 80 vol % ethanol solution of GMA monomer of 1.0M at 60°C. The PE-g-PGMA films of the grafted amount of 14.1 mmol/g-PE were immersed in an aqueous DMSO solution of 0.425M IDA2Na. The DMSO volume fraction ranged from 40 to 55 vol %. Epoxy groups appended to the grafted PGMA chains were converted into IDA groups by heating the solutions in which the PE-g-PGMA films were immersed at 80°C for 24 h with moderate stirring. Figure 1 shows the change in the conversion with the DMSO volume fraction of the solvent for a PE-g-PGMA film of 14.1 mmol/g-PE. The conversion from epoxy into IDA groups increased with an increase in the volume fraction of DMSO. The presence of DMSO in the solution is considered to enhance the reactivity of an epoxy group with IDA2Na through the mechanism of SN2.[30] However, IDA2Na was less soluble in the aqueous DMSO solutions of the volume fraction more than 60
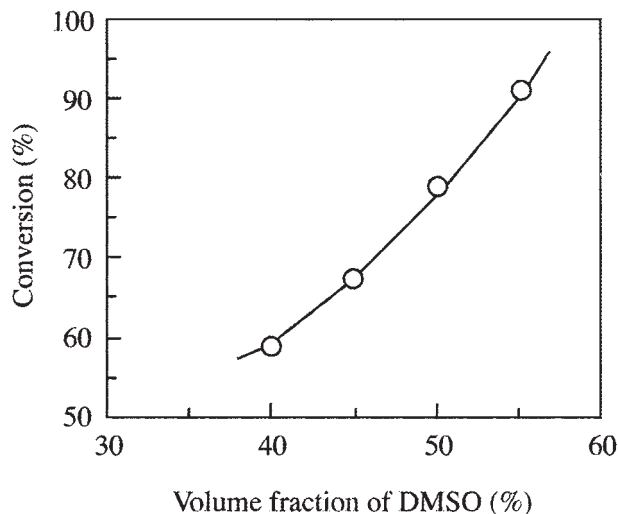
Figure 1 Change in the conversion with the volume fraction of DMSO of the solvent. Reaction was carried out at 80°C for 24 h. The grafted amount of the PE-g-PGMA films used was 14.1 mmol/g.

vol %. Therefore, an aqueous 55 vol % DMSO solution was used as the solvent for the preparation of the IDA-(PE-g-PGMA) films.

The PE films were expanded by the photografting of GMA like the PE films photografted with MAA, AA, DMAEMA, and NIPAAm.[2-6] The subsequent conversion of epoxy groups into IDA groups caused the PE-g-PGMA films to expand more, because the introduction of IDA groups conferred the water-absorptivity to the PE-g-PGMA films. Figure 2 shows the changes in the area ratio with the grafted amount (the original size before photografting = 3.0×6.0 cm^2). The PE films were expanded by the photografting of GMA, and their area ratios increased with an increase in the grafted amount. This result indicates that the internal grafting, which occurs simultaneously with the surface grafting, causes the PE film expand.[2,6] The area ratios of the PE-g-PGMA films were higher than those of the PE films photografted with MAA, AA, MAAm, and DMAEMA in the water-swollen state, although the PE-g-PGMA films showed hardly any water absorption. This suggests that the internal grafting progresses more for the photografting of GMA than for those of hydrophilic monomers. The PE-g-PGMA films were further expanded because of the increasing hydrophilization of the PE-g-PGMA films by the introduction of IDA groups (conversion: ~90%). Figure 3 shows the changes in the amount of absorbed water and n_{water} value with the grafted amount for IDA-(PE-g-PGMA) films. Here, the n_{water} value represents the number of water molecules assigned to one IDA group or IDA-appended GMA monomer segment for the IDA-(PE-g-PGMA) films, and was calculated from the amounts of absorbed water and of introduced IDA groups from eq. (3) in
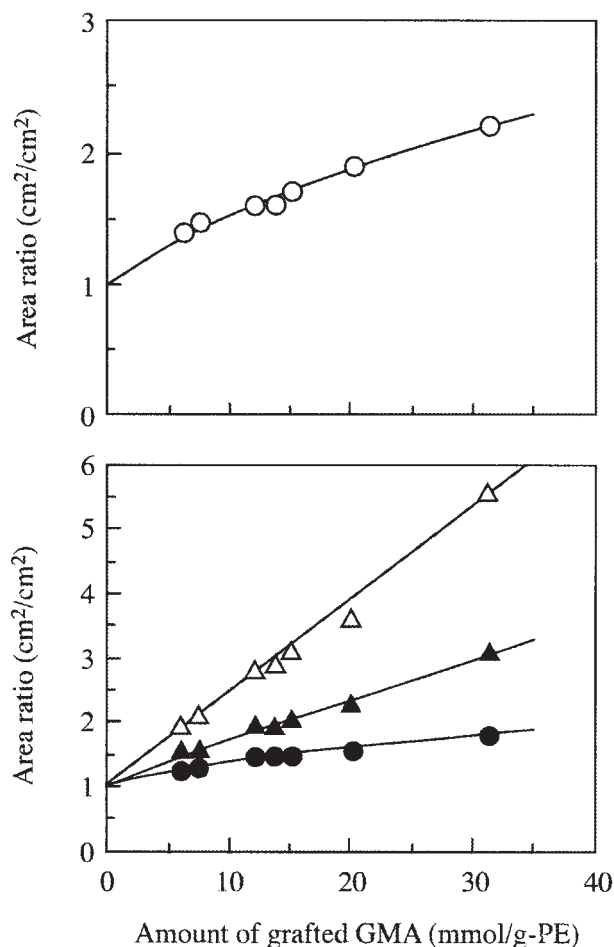
Figure 2 Changes in the area ratio (cm^2/cm^2) with the amount of grafted GMA. Dry PE-g-PGMA/PE (○), swollen IDA-(PE-g-PGMA)/PE (△), Dry IDA-(PE-g-PGMA)/Dry PE-g-PGMA (▲), Swollen IDA-(PE-g-PGMA)/dry IDA-(PE-g-PGMA) (●).
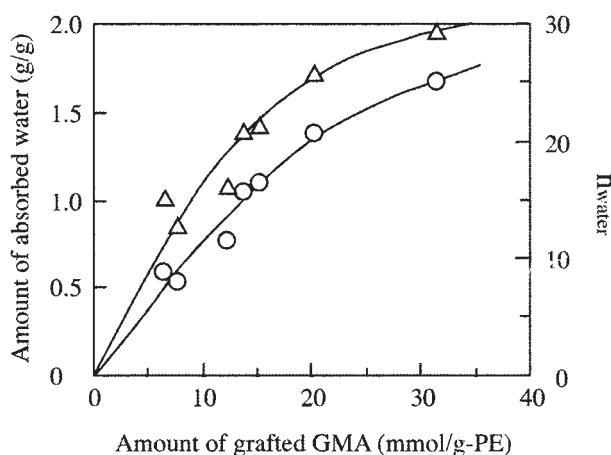
Figure 3 Changes in the amount of absorbed water (○) and n_{water} value (△) with the amount of grafted GMA of the IDA-(PE-g-PGMA) films with the conversion of ~90%.

reference 8 to discuss their water-absorptivity in more detail.[3,8] The n_{water} value as well as the amount of absorbed water for the IDA-(PE-g-PGMA) films increased with an increase in the grafted amount. The increase in the n_{water} value indicates that the water-absorptivity of the IDA-(PE-g-PGMA) films increases over the grafted amount. As described in references 3 and 8, a constant n_{water} value is obtained in the case where the water-absorptivity of the grafted films linearly increased with the grafted amount. It was found from Figures 2 and 3 that the introduction of IDA groups to the PE-g-PGMA films offered the water absorptivity in addition to further expansion of the PE-g-PGMA films. The water-absorptivity is considered to play an important role in applying the IDA-(PE-g-PGMA) films to the chelating membranes for adsorption of metal ions. The detailed experimental results will be described below.

In the paper reported by Yamaguchi et al., the maximum conversion of epoxy groups into IDA groups was limited to 60–65%.[30] Therefore, after the introduction of IDA groups, the remaining epoxy groups were converted into alcoholic dihydroxyl groups with sulfuric acid to enhance the hydrophilicity of the GMA-grafted porous membranes. In this study, the conversion into IDA groups went up to 90% by prolonging the reaction time to 24 h as well as by increasing the volume fraction of DMSO in the solvent to 55 vol %. Since the IDA-(PE-g-PGMA) films with the conversion of more than 90% possessed high water-absorptivity as shown in Figure 3, the IDA-(PE-g-PGMA) films were used on adsorption experiments without converting the remaining epoxy groups.

Cu²⁺ ion adsorption properties of IDA-(PE-g-PGMA) film

The grafted amount dependence

The amount of Cu^{2+} ions adsorbed on IDA-(PE-g-PGMA) films with the grafted amounts of 10–50 mmol/g-PE was measured at the prescribed time intervals in an 1.0 mM $CuCl_2$ buffer of pH 5.0 at 30°C. The IDA-(PE-g-PGMA) films used in this section had the average conversion of 90.7%. The amount of adsorbed Cu^{2+} ions increased with an increase in the immersion time, and then leveled off. The degree of adsorption for each IDA-(PE-g-PGMA) film was calculated from the amount of adsorbed Cu^{2+} ions at equilibrium and the degree of conversion into IDA groups. In addition, the kinetic constants of adsorption were calculated from the slope of the linear relationship between the immersion time and ln $(1-Q_t/Q_{eq})$ value.[32,33] Here, the adsorption of Cu^{2+} ions on the IDA-(PE-g-PGMA) films was assumed to proceed like a first-order reaction, and the kinetic constants of adsorption, k, were calculated using eq. (1):
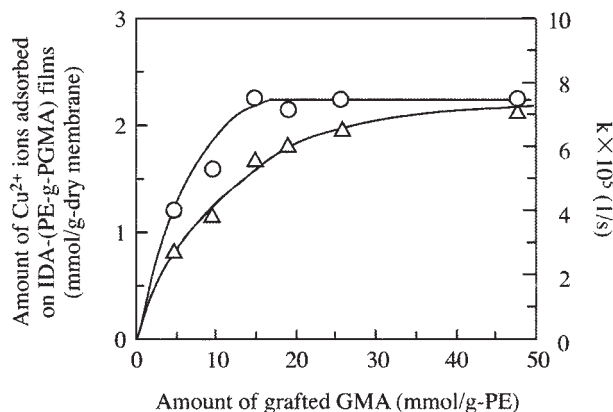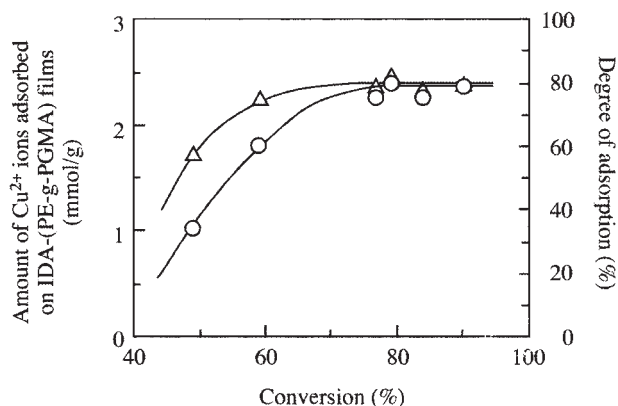

Figure 4 Changes in the amount of adsorbed Cu^{2+} ions (○) and the value of the kinetic constant of adsorption (△) with the amount of grafted GMA at pH 5.0 and 30°C in the initial $CuCl_2$ concentration of 1.0 mM.

$$\ln\left(1 - \frac{Q_t}{Q_{eq}}\right) = -k \cdot t \tag{1}$$

where Q_t and Q_{eq} were the amount of adsorbed Cu^{2+} ions at the immersion time t and equilibrium, respectively. Figure 4 shows the dependence of the Cu^{2+} ion adsorption on the grafted amount at 30°C. The amount of adsorbed Cu^{2+} ions increased with an increase in the grafted amount, and then stayed constant in the range of the grafted amounts of >15 mmol/g-PE. The kinetic constant of adsorption was also plotted as a function of the amount of grafted GMA in Figure 4. The value of the kinetic constant of adsorption increased even at >15 mmol/g-PE. Since the IDA-(PE-g-PGMA) films possess good water-absorptivity as shown in Figure 3, the IDA group-appending grafted PGMA chains are expected to have considerably high mobility in the water-swollen state. The high water-absorptivity of the IDA-(PE-g-PGMA) films is considered to lead to the increase in the kinetic constant of adsorption, but the degree of adsorption was limited to 80%. This is probably due to the restriction of diffusion of Cu^{2+} ions to the inner sides of the grafted layers. It was found from the above results that a considerable amount of Cu^{2+} ions were effectively adsorbed on the IDA-(PE-g-PGMA) films with higher grafted amounts without a decrease of the rate of adsorption.

The IDA group conversion dependence

The Cu^{2+} ion adsorptivity was estimated in an 1.0 mM $CuCl_2$ buffer at pH 5.0 and 30°C for the IDA-(PE-g-PGMA) films of the grafted amount of 14–15 mmol/g-PE with different conversions from 40 to 93%. Figure 5 shows the changes in the amount of adsorbed Cu^{2+} ions and the degree of adsorption with the conversion.

Figure 5 Changes in the amount of adsorbed Cu^{2+} ions (○) and the degree of adsorption (△) with the conversion at pH 5.0 and 30°C for the IDA-(PE-g-PGMA) films of the grafted amount of 14–15 mmol/g-PE at the initial $CuCl_2$ concentration of 1.0 mM.

The amount of adsorbed Cu^{2+} ions increased with the conversion, and then stayed constant at conversion more than about 80%. The increase in the conversion leads to the increase in the water-absorptivity of the IDA-(PE-g-PGMA) films in addition to the net amount of IDA groups as a chelate-forming functional group as shown in Figure 3. This result supports our view that the increase in the water-absorptivity caused by the increase in the conversion has a favorable influence on the increase in the diffusivity of Cu^{2+} ions into the IDA-(PE-g-PGMA) films. In addition, the increase in the degree of adsorption against the conversion means that IDA groups in the inside of the IDA-g-(PE-g-PGMA) films also effectively work for chelate formation to Cu^{2+} ions at higher conversions. From the above experimental results, the dependence of Cu^{2+} ion adsorption on the pH value, $CuCl_2$ concentration, and temperature was investigated for an IDA-(PE-g-PGMA) film with the conversion of ~90%.

The pH value dependence

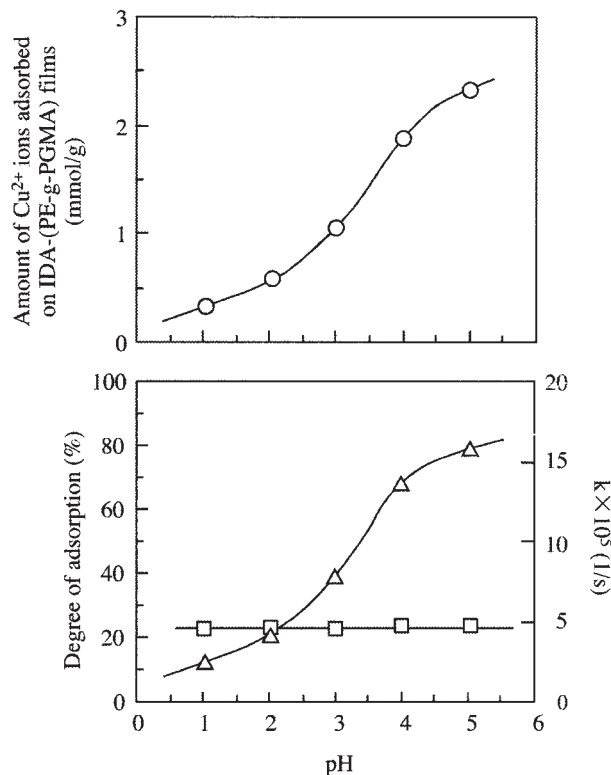The IDA-(PE-g-PGMA) films of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7% were immersed in the 1.0 mM $CuCl_2$ buffers in the pH range of 1.0–5.0 at 30°C. Figure 6 shows the pH dependence of Cu^{2+} ion adsorption. Although the amount of adsorbed Cu^{2+} ions and the degree of adsorption increased with an increase in the pH value, the value of the kinetic constant of adsorption stayed almost constant (4–5 $\times$ 10^{-5} s^{-1}) against the pH value. The increase in the pH value promotes the dissociation of the IDA groups from —N(COOH)$_2$ to —N(COO$^-$)$_2$ forms that are responsible for the chelating adsorption of Cu^{2+} ions. This result indicates that the rate of chelating adsorption of Cu^{2+} ions to —N(COO$^-$)$_2$ groups is independent of the pH value.

The $CuCl_2$ concentration dependence

From the experimental results of the pH dependence of Cu^{2+} ion adsorption shown in Figure 6, the dependence of Cu^{2+} ion adsorption on the $CuCl_2$ concentration was investigated at pH 5.0 and 30°C. Figure 7 shows the $CuCl_2$ concentration dependence of Cu^{2+} ion adsorption for an IDA-(PE-g-PGMA) film of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7%. The amount of adsorbed Cu^{2+} ions and degree of adsorption increased with an increase in the initial $CuCl_2$ concentration, in particular, it sharply increased below 0.5 mM. The value of the kinetic constant of adsorption slightly increased from 4.0 $\times$ 10^{-5} to 6.5 $\times$ 10^{-5} s^{-1} in the initial $CuCl_2$ concentration ranging from 0.05 to 2.0 mM. The adsorption of Cu^{2+} ions on the IDA-(PE-g-PGMA) films was analyzed according to the Langmuir adsorption isotherm equation:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q} \cdot b + \frac{C_{eq}}{Q} \tag{2}$$

where C_{eq} is the free Cu^{2+} ion concentration in the surrounding solution at equilibrium; Q, the maximum

Figure 6 Changes in the amount of adsorbed Cu^{2+} ions (○), the degree of adsorption (△), and the value of the kinetic constant of adsorption (□) with the pH value at 30°C for an IDA-(PE-g-PGMA) film of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7% at the initial $CuCl_2$ concentration of 1.0 mM.
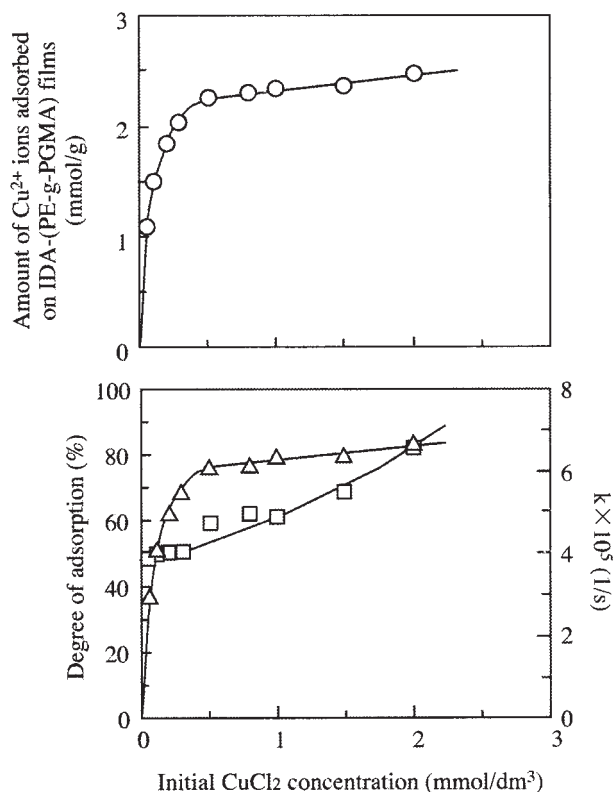
Figure 7 Changes in the amount of adsorbed Cu^{2+} ions ($\bigcirc$), the degree of adsorption ($\triangle$) and the value of the kinetic constant of adsorption ($\square$) with the initial $CuCl_2$ concentration at pH 5.0 and 30°C for an IDA-(PE-g-PGMA) film of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7%.

amount of adsorbed Cu^{2+} ions; and *b*, the Langmuir constant. The equilibrium $CuCl_2$ concentration and the amount of adsorbed Cu^{2+} ions bore a linear relationship in Langmuir adsorption isotherm equation with the Langmuir constant of 29.9 dm^3/mol.[33–36] This result indicates that Cu^{2+} ions are bonded to IDA groups in the 1:1 stoichiometry through the chelating mechanism. The adsorption of Cu^{2+} ions on the IDA-(PE-g-PGMA) films was assumed to proceed like a first-order-reaction.

The temperature dependence

The temperature dependence of Cu^{2+} ion adsorption was investigated in an 1.0 m*M* $CuCl_2$ buffer of pH 5.0 since the amount of adsorbed Cu^{2+} ions had maximum value at pH 5.0 in the range of the pH values from 1.0 to 5.0 as shown in Figure 6. Figure 8 shows the changes in the degree of adsorption and the time required to reach the equilibrium adsorption with the temperature. The time required to the reach the equilibrium adsorption was shortened with the temperature, although the degree of adsorption stayed constant and the value of the kinetic constant of adsorp-

tion increased with the temperature. When the values of the kinetic constant of adsorption obtained from the slope of the straight line between ln $(1-Q_t/Q_{eq})$ and the immersion time at each temperature was plotted in accordance with the Arrhenius equation as ln k versus $1/T$, the activation energy of 38.5 kJ/mol was estimated from the linear relationship. The fact that the data plots fall on a straight line implies that the activation energy is a constant independent of the temperature.

Dependence of Cu^{2+} ion desorption on the HCl concentration

The effect of HCl concentration on desorption of Cu^{2+} ions was investigated by immersing the IDA-(PE-g-PGMA) films (grafted amount = 15.3 mmol/g-PE, conversion = 91.6%), which had reached the equilibrium adsorption in the aqueous HCl solutions of 0.05–1.0*M* at 30°C. The amount of Cu^{2+} ions desorbed from the IDA-(PE-g-PGMA) films increased with an increase in the immersion time, and then leveled off irrespective of the HCl concentration.[29,36] Figure 9 shows the changes in the degree of desorption determined as the ratio of the desorbed amount to the adsorbed amount and the time required to reach the
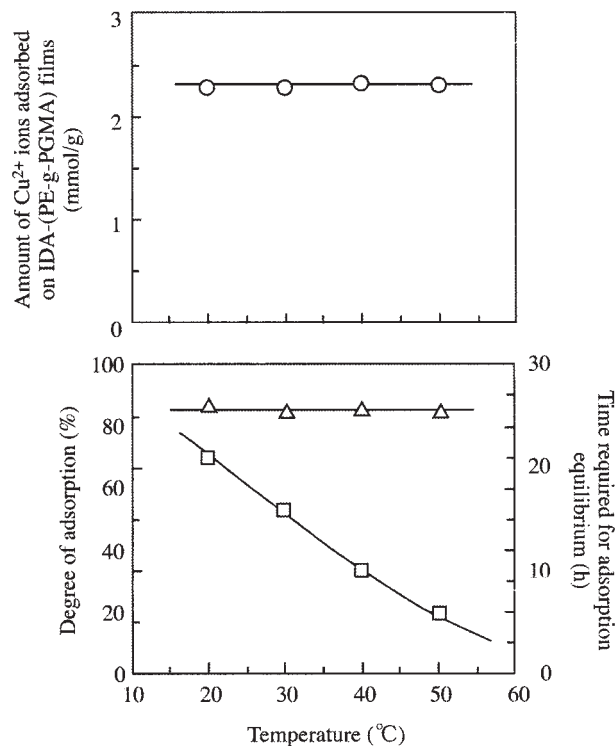
Figure 8 Changes in the amount of adsorbed Cu^{2+} ions ($\bigcirc$), the degree of adsorption ($\triangle$), and the time required for adsorption equilibrium ($\square$) with the temperature at pH 5.0 for an IDA-(PE-g-PGMA) film of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7% at the initial $CuCl_2$ concentration of 1.0 m*M*.
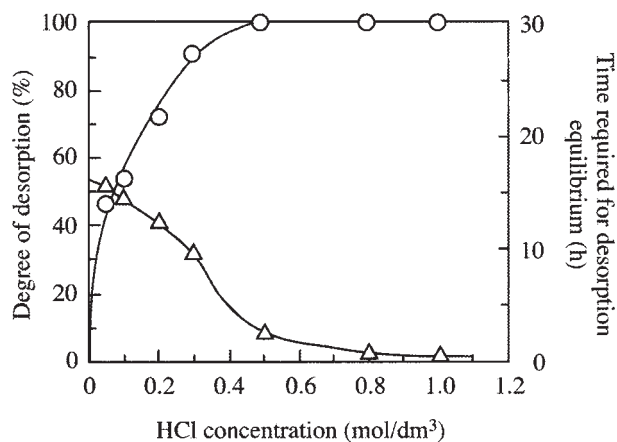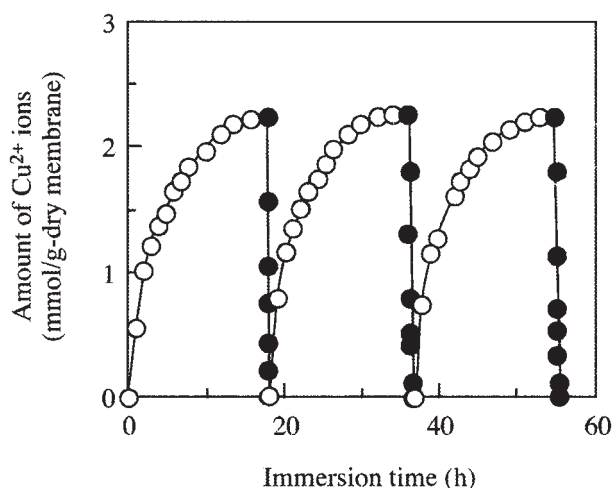
Figure 9 Changes in the degree of desorption (○) and the time required for desorption equilibrium (△) with the HCl concentration for an IDA-(PE-g-PGMA) film of the grafted amount of 14.1 mmol/g-PE with the conversion of 90.7% at 30°C.

Figure 10 The alternately repeated cyclic processes of adsorption of Cu^{2+} ions (○) in a $CuCl_2$ buffer at pH 5.0 and desorption of Cu^{2+} ions (●) in an aqueous 1.0M HCl solution.

equilibrium desorption with the HCl concentration. The degree of desorption increased with an increase in the HCl concentration. In the aqueous HCl solutions of more than 0.5M, the majority of Cu^{2+} ions were desorbed from the IDA-(PE-g-PGMA) films and the time required to reach the equilibrium desorption was shortened with an increase in the HCl concentration. Since the chelation takes place between a dissociated IDA (—N(COO$^-$)$_2$) group and a Cu^{2+} ion, the increase in the HCl concentration causing the depression of the dissociation of IDA groups from —N(COO$^-$)$_2$ to —N(COOH)$_2$ form leads to the increase in the desorption of Cu^{2+} ions.

Repetitive cycles of adsorption and desorption

On the basis of the results on the pH dependence of both adsorption of Cu^{2+} ions as shown in Figure 6 and their desorption as shown in Figure 9, the cyclic process of adsorption at pH 5.0 and desorption in an 1.0M HCl solution was alternately repeated for the IDA-(PE-g-PGMA) film with the grafted amount of 15.3 mmol/g-PE and the conversion of 91.6%.[29,33] Figure 10 shows the three successive Cu^{2+} ion adsorption–desorption cycles. When the IDA-g-(PE-g-PGMA) film was put back in a $CuCl_2$ buffer at pH 5.0 after the first desorption process, Cu ions were adsorbed on the IDA-(PE-g-PGMA) film to almost the same adsorbed amount in the first adsorption process. The adsorption and desorption behavior was almost equivalent in each cyclic process. It is found from Table I that the IDA-(PE-g-PGMA) film is 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 IDA-g-(PE-g-PGMA) films to Cu^{2+} ions and their repetitive cycles of adsorption and desorption. From the experimental results above, we can conclude the following:

The conversion of epoxy into IDA groups goes up to 90% by prolonging the reaction time as well as by increasing the volume fraction of DMSO in the solvent to 55 vol %. The introduction of IDA groups yields the high water-absorptivity to the PE-g-PGMA films. The degree of adsorption of Cu^{2+} ions increases with an increase in the pH value in the range of 1.0–5.0 and the time required to reach the equilibrium adsorption is shortened by the increase in the temperature. The degree of desorption increases and the time required for the desorption equilibrium is shortened with an increase in the HCl concentration and the majority of Cu^{2+} ions are desorbed in the aqueous HCl solutions at more than 0.5M. The cyclic process of adsorption at

TABLE I
Physicochemical Properties of the Alternately Repeated Cyclic Processes of Adsorption in a $CuCl_2$ Buffer at pH 5.0 and Desorption in an Aqueous 1.0M HCl Solution

Run number	1	2	3
Amount of adsorbed Cu^{2+} ions (mmol/g-dry membrane)	2.24	2.27	2.25
Degree of adsorption (%)	78.8	79.7	79.1
Kinetic constant of adsorption ($\times 10^5$ s^{-1})	5.48	5.9	5.68
Degree of desorption (%)	99.6	98.9	99.7
Kinetic constant of desorption ($\times 10^5$ s^{-1})	703	678	698

pH 5.0 and desorption in 1.0M HCl solution is alternately repeated without considerable fatigue. It is made clear from the above results that the IDA-(PE-g-PGMA) films are used as a repeatedly generative chelating membrane for metal ions.

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