

Formation of Thermosensitive Copolymer Beads Having Phosphinic Acid Groups and Adsorption Ability for Metal Ions

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ABSTRACT: Hydrophilic thermosensitive copolymer beads having phosphinic acid groups were prepared by suspension copolymerization of acryloyloxypropyl *n*-octylphosphinic acid (APPO), *N*-isopropyl acrylamide (NIPAAm), and tetraethyleneglycol dimethacrylate (4G). The thermosensitivity and the adsorption ability of the copolymer beads for metal ions were studied. The APPO-NIPAAm-4G copolymer beads were obtained in a good yield by suspension copolymerization of monomers (APPO, NIPAAm, and 4G) dissolved in chloroform, in a saturated Na₂SO₄ aqueous solution in the presence of surfactant and MgCO₃. The APPO-NIPAAm-4G copolymer beads had higher adsorption ability for lanthanide metal ions (Eu³⁺, Sm³⁺, Nd³⁺, or La³⁺) than for main transition

metal ions (Cu²⁺, Ni²⁺, or Co²⁺). Furthermore, it was also found that the APPO-NIPAAm-4G copolymer beads had selective adsorption ability between lanthanide metal ions, and the order of adsorption ability for lanthanide metal ions was as follows: Eu³⁺ > Sm³⁺ > Nd³⁺ > La³⁺. The selective adsorption for these metal ions from their mixed solutions was performed by both a batch method and a column method. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 449–460, 2006

Key words: stimuli-sensitive polymers; adsorption; metal-polymer complexes; acryloyloxypropyl *n*-octylphosphinic acid; *N*-isopropylacrylamide

INTRODUCTION

Poly(*N*-isopropylacrylamide) (NIPAAm) is a thermosensitive polymer having a lower critical solution temperature (LCST) at around 32°C in an aqueous solution, that is, polyNIPAAm dissolves in water below LCST and does not dissolve above LCST. The copolymers containing polyNIPAAm have been widely studied from fundamental and practical points of views.^{1–15} We previously reported that water-soluble thermosensitive copolymers consisting of acryloyloxypropyl phosphinic acid (APPA) and NIPAAm had adsorption ability for lanthanide metal ions or main transition metal ions, in particular, they had higher adsorption ability for lanthanide metal ions than for main transition metal ions.¹⁶ And the APPA-NIPAAm copolymer-metal complexes exhibited high thermosensitivity and different thermosensitive behavior depending on kinds of metal ions adsorbed,¹⁶ although the APPA-NIPAAm copolymers had only low thermosensitivity because of the introduction of phosphinic acid groups. Furthermore, we also found

that selective removal of lanthanide metal ions, from their mixed solutions containing main transition metal ions, could be performed, by changing the temperature of the solution, in which the copolymer-metal complexes were formed. In this study, acryloyloxypropyl *n*-octylphosphinic acid (APPO), which has more hydrophobic *n*-octyl group in phosphinic acid group, was used instead of APPA. This report is concerned with the preparation of crosslinked thermosensitive copolymer beads having phosphinic acid groups by the suspension copolymerization of APPO, NIPAAm, and tetraethyleneglycol dimethacrylate (4G), and the selective adsorption ability of the APPO-NIPAAm-4G copolymer beads obtained for metal ions, in particular, for lanthanide metal ions, was measured by a batch method and a column method.

EXPERIMENTAL

Materials

APPO and NIPAAm were kindly supplied by Nippon Kagaku Kogyo (Tokyo, Japan) and Kohjin (Tokyo, Japan), respectively, and APPO was used without further purification. NIPAAm was purified by recrystallization from tetrahydrofuran/*n*-hexane mixture. Tet-

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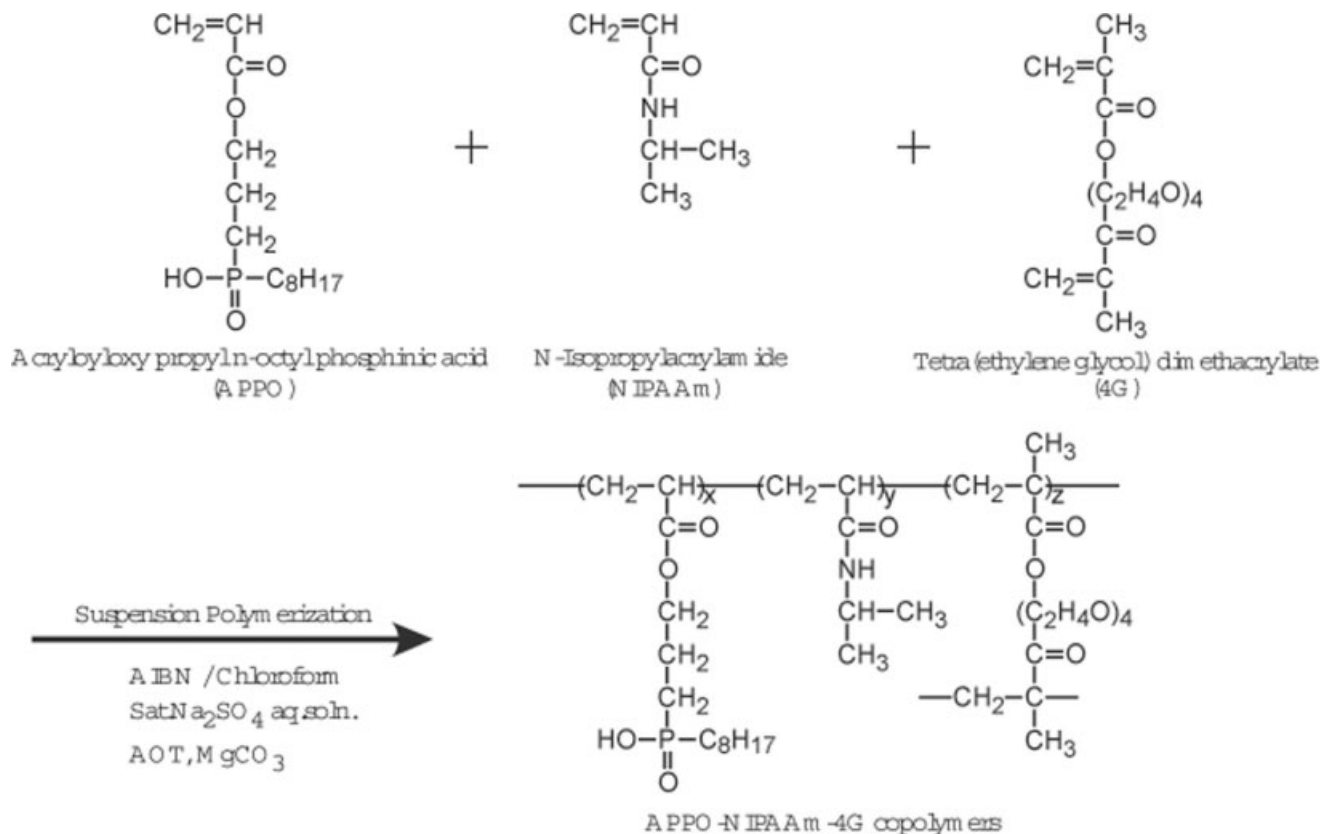


Figure 1 Synthesis of APPO-NIPAAm-4G copolymer beads.

raethyleneglycol dimethacrylate (4G), as a crosslinking reagent, was purchased from Sigma-Aldrich Japan (Tokyo, Japan) and was used without further purification. α,α' -Azobisisobutyronitrile (AIBN) (Nacal Tesque, Tokyo, Japan) was purified by recrystallization from ethanol (Wako Pure Chemical Industries, Osaka, Japan). Other chemical compounds were reagent grade and were used as received.

Synthesis of crosslinked APPO-NIPAAm-4G copolymer beads

The structure of APPO-NIPAAm-4G copolymer beads is shown in Figure 1. First, total amount (4 g) of APPO, NIPAAm, and 4G was dissolved in 4 g of chloroform, and to this solution, AIBN (15 mg) was dissolved under a nitrogen atmosphere. The mixed monomer solution prepared was dispersed into a saturated Na_2SO_4 aqueous solution (400 mL) containing 0.1 g of surfactant (AOT, sodium sulfodiisooctyl succinate) and 4 g MgCO_3 in three necked separable round bottom flask equipped with condenser, stirrer, and nitrogen inlet. Polymerization was carried out with stirring at 400 rpm at 50°C for 3 h, and further at 60°C for 1 h under a nitrogen atmosphere. After polymerization, the product was filtered off and refluxed with pro-

panone for 12 h. Then, the product was alternately soaked in water of 10°C and 60°C to remove unreacted monomers from the product. After drying, the copolymer beads were used for experiments. The content of phosphinic acid groups in the copolymer beads was calculated from the phosphorus content of the dried copolymer beads. The phosphorus content was determined as follows: Dried copolymer beads (0.1 g) and 70% nitric acid (10 mL) were placed in a Kjeldahl flask and the mixture was heated until white steam came out, and was then cooled. After that, 60% perchloric acid (10 mL) was added to this solution, and the mixture was heated until the solution became transparent. The concentration of phosphoric acid in the resulted solution was determined by phosphovanadomolybdate method.¹⁷ The nitrogen content, which corresponds to the NIPAAm content in the copolymer beads, was determined by the elemental analysis (Yanaco CHN Corder MT-6).

Measurement of the swelling volume of the APPO-NIPAAm-4G copolymer beads

Dried copolymer beads (0.2 g) were soaked for 24 h at room temperature ($24\text{--}25^\circ\text{C}$) in deionized water in 5 mL measuring cylinder, and then the temperatures

TABLE I
Conditions for the Preparation of APPO-NIPAAm-4G Copolymer Beads

APPO : NIPAAm : 4G (molar ratio in feed)	Initiator	Surfactant	Dispersant	Rotation speed (rpm)	Temp. (°C)	Particles
5 : 97 : 3	AIBN ^a	—	—	360	50	Blocky
5 : 97 : 3	AIBN	—	PEG6500K	360	50	Blocky
5 : 97 : 3	AIBN	—	PEG20K	360	50	Blocky
5 : 97 : 3	AIBN	—	PVP	360	50	Blocky
5 : 97 : 3	BPO + TMEDA	—	—	360	30	Blocky
5 : 97 : 3	BPO + DMA	—	—	360	30	Blocky
5 : 97 : 3	AIBN	AOT	—	360	50	Blocky
10 : 97 : 3	AIBN	AOT	—	360	50	Blocky
15 : 97 : 3	AIBN	AOT	—	360	50	Blocky
15 : 97 : 3	AIBN	AOT	MgCO ₃	300	50	Spherical

Saturated sodium sulfate solution was used as the dispersion medium, and chloroform was used as solvent for monomers in all the experiments.

AIBN, α,α' -azobisisobutyronitrile; BPO, benzoylperoxide; TMEDA, *N,N,N',N'*-tetramethyl ethylenediamine; DMA, *N,N*-dimethylaniline; AOT, sodium sulfo diisooctyl succinate; PEG, poly(ethyleneglycol); PVP, poly(vinyl pyrrolidone).

was varied and the copolymer beads were allowed to stand at each temperature for 1 h. The swelling volume of the copolymer beads at each temperature was calculated using eq. (1).

$$\text{Swelling volume (mL g}^{-1}\text{)} = \frac{\text{Apparent volume (mL)}}{\text{Weight of copolymer beads (g)}} \quad (1)$$

Measurement of the adsorption capacity of the copolymer beads for metal ions

Dried copolymer beads (0.1 g) were placed into 25 mL of each pH buffer solution in 50 mL Erlenmeyer flask, and the flask was shaken at desired temperatures for 24 h to complete the swelling of the copolymer beads. And then, 25 mL of metal ion solution were powered into the flask and shaken for further 24 h at desired temperatures. After that, the copolymer beads were filtered. The adsorption capacity was calculated by determining the concentration of residual metal ions in the supernatant with inductively coupled argon plasma atomic emission spectrophotometer (Shimadzu ICPS-5000). To investigate the temperature dependence of the adsorption of metal ions with the copolymer beads, the aforementioned procedure was carried out at various temperatures.

Column method for the adsorption or elution of metal ions

Dried copolymer beads (20 g) were placed in a glass column (10 mm in diameter) and were completely swollen at 25°C for 24 h. A metal ion solution of 0.25 mol L⁻¹ was passed through the column of the swollen copolymer beads at a velocity of 1.0 mL min⁻¹. Each 5 mL aliquot of effluent was collected until 500 mL. After adsorption experiment, the column was

washed with deionized water until the metal ion in washing water became undetectable. The metal ions adsorbed were eluted by passing 1 mol L⁻¹ HCl solution through the column at the velocity of 1.0 mL min⁻¹. Each 3 mL aliquot of acid eluate was collected until 81 mL. The metal concentration in each aliquot of effluent and acid eluate was determined with inductively coupled argon plasma atomic emission spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of the APPO-NIPAAm-4G copolymer beads

NIPAAm is an amphoteric monomer, and APPO and 4G are not water-soluble monomers. Therefore, it is very difficult to obtain spherical copolymer beads consisting of these three monomers by usual radical suspension copolymerization in water. We tried to obtain spherical copolymer beads by suspension polymerization under various conditions. Table I shows the monomer ratios in feed and various conditions for suspension copolymerization. The molar ratio of APPO to NIPAAm + 4G (NIPAAm:4G = 97 : 3 molar ratio) was varied from 5 to 15. AIBN or redox initiators (benzoyl peroxide + *N,N,N',N'*-tetramethyl ethylenediamine or benzoyl peroxide + *N,N*-dimethylaniline) were used as initiators. A saturated Na₂SO₄ aqueous solution was used as a dispersing medium. Poly(ethyleneglycol) or poly(vinyl pyrrolidone) dissolved in water was used as an auxiliary dispersing agent in the absence or the presence of surfactant (AOT, sodium sulfodiisooctyl succinate). It was found that spherical copolymer beads could be prepared in a good yield by suspension copolymerization of monomers (APPO, NIPAAm, and 4G) dissolved in chloro-

TABLE II
Content of Phosphorus in APPO-NIPAAm-4G
Copolymer Beads

No. of copolymer beads	APPO : NIPAAm : 4G (molar ratio in feed)	P content in copolymer beads	
		Found (mmol g ⁻¹)	Calcd. (mmol g ⁻¹)
1	5 : 97 : 3	0.22	0.37
2	10 : 97 : 3	0.41	0.67
3	15 : 97 : 3	0.56	0.92
4	10 : 95 : 5	0.40	0.65
5	15 : 95 : 5	0.54	0.90
6	20 : 95 : 5	0.67	1.10
7	15 : 90 : 10	0.47	0.84
8	20 : 90 : 10	0.60	1.04
9	30 : 90 : 10	0.81	1.35

Copolymer beads were prepared by suspension copolymerization in saturated sodium sulfate solution in the presence of surfactant (AOT) and MgCO₃ at 50°C for 4 h at 300 rpm.

form, in a saturated Na₂SO₄ aqueous solution in the presence of AOT and magnesium carbonate. AOT and basic light magnesium carbonate were used as auxiliary dispersing agents. Table II shows the monomer ratios in feed and the content of phosphorous in the APPO-NIPAAm-4G copolymer beads obtained. The molar ratios of APPO to NIPAAm + 4G (100 molar ratio) in feed were varied from 5 to 30 molar ratios and the molar ratios of 4G in NIPAAm + 4G (100 molar ratio) were varied from 3 to 10. The copolymer beads having different phosphorous content could be easily prepared by varying the APPO content in the feed. However, the phosphorous contents in the copolymers obtained under these polymerization conditions were about 60% of the calculated values. Figure 2 shows the scanning electron micrograph of the APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads obtained. The perfect spherical copolymer beads were not obtained yet, under these polymerization conditions. The diameter of the beads obtained was less than 100 μm.

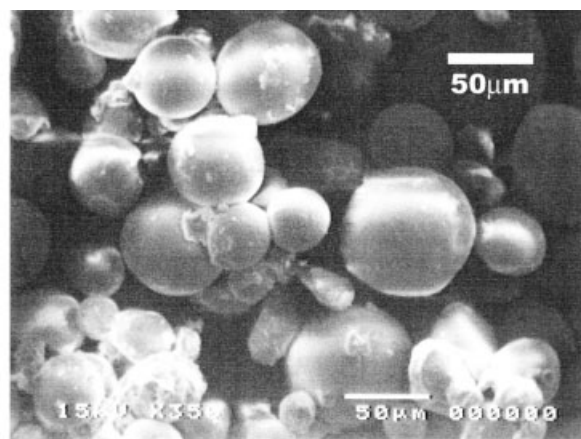
Temperature dependence of the swelling volume of the APPO-NIPAAm-4G copolymer beads

The swelling volume (mL g⁻¹) of the copolymer beads, which were obtained by varying the contents of APPO and crosslinking reagent in feed, was measured in deionized water at various temperatures. The results are shown in Figure 3. In each copolymer bead obtained at different content of crosslinking agent [Figs. 3(a–c)], it was found that the swelling volume decreased with increasing temperature. The decrease in the swelling volume of the copolymer beads with increasing temperature is due to the thermosensitivity

of polyNIPAAm moieties in the copolymers. Furthermore, it was found that the swelling volume of the copolymer beads, which were obtained at the same molar ratio of 4G in feed, increased with increasing APPO content in the copolymer beads. This indicates that the difference of osmotic pressure between the inner side and outer side of the copolymer beads in deionized water became larger, as the content of phosphinic acid groups in the copolymer beads increased. The degree of the decrease in the swelling volume of the APPO-NIPAAm-4G (X : 97 : 3) copolymer beads with increasing temperature was larger than those of other APPO-NIPAAm-4G ((X : 95 : 5) and (X : 90 : 10)) copolymer beads containing higher 4G content. Furthermore, the swelling volume of the APPO-NIPAAm-4G ((X : 97 : 3), (X : 95 : 5), and, (X : 90 : 10)) copolymer beads leveled off above about 30, 25, and 20°C, respectively. This indicates that increasing content of 4G (crosslinking reagent) in the copolymer beads made the copolymers more hydrophobic. Thus, it was found that the swelling volume of the copolymer beads was not only affected by the APPO content and the degree of crosslinking in the copolymer beads but also by the temperature measured.

Effect of temperature on the adsorption of metal ions with the APPO-NIPAAm-4G copolymer beads

The APPO-NIPAAm-4G copolymer beads have phosphinic acid groups, which are known to be able to coordinate with metal ions, in particular, with lanthanide ions.^{18–20} As mentioned earlier, the swelling volume of the APPO-NIPAAm-4G (10 : 97 : 3) copolymer beads in water decreased with increasing temperature. Therefore, the adsorption ability of the copoly-



APPO-NIPAAm-4G copolymer beads

Figure 2 Scanning electron micrograph of APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads obtained by suspension polymerization.

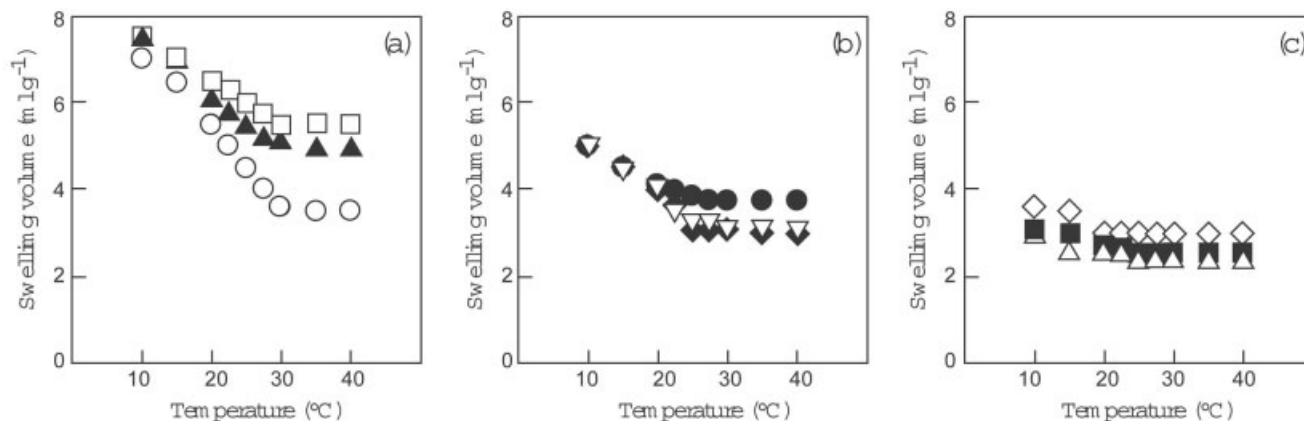


Figure 3 Temperature dependence of the swelling volume of APPO-NIPAAm-4G copolymer beads in deionized water. Copolymers: (a) APPO-NIPAAm-4G (X : 97 : 3), X-5 (○), 10 (▲), 15 (□); (b) APPO-NIPAAm-4G (X : 95 : 5), X-10 (◆), 15 (▽), 20 (●); (c) APPO-NIPAAm-4G (X : 90 : 10), X-15 (△), 20 (■), 30 (◇).

mer beads for Sm^{3+} was measured by shaking for 24 h at various temperatures (10, 20, and 30°C) at pH 6.5. The figure for the results was omitted. Usually, the metal adsorption ability of adsorptive resins such as chelating ion exchange has been measured at room temperature (24–25°C), because the adsorption ability was not affected significantly by temperature. However, the APPO-NIPAAm-4G (10 : 97 : 3) copolymer bead showed the maximum adsorption ability for Sm^{3+} at 20°C, although the difference in the adsorp-

tion ability between at 10°C and 30°C was very small. The small decrease in the adsorption ability for Sm^{3+} at 30°C is due to the shrinkage of the copolymer beads in water at that temperature.

Effect of pH on the adsorption of metal ions with the APPO-NIPAAm-4G copolymer beads from its single metal ion solution

First, the adsorption ability of the APPO-NIPAAm-4G copolymer beads, which have different APPO content

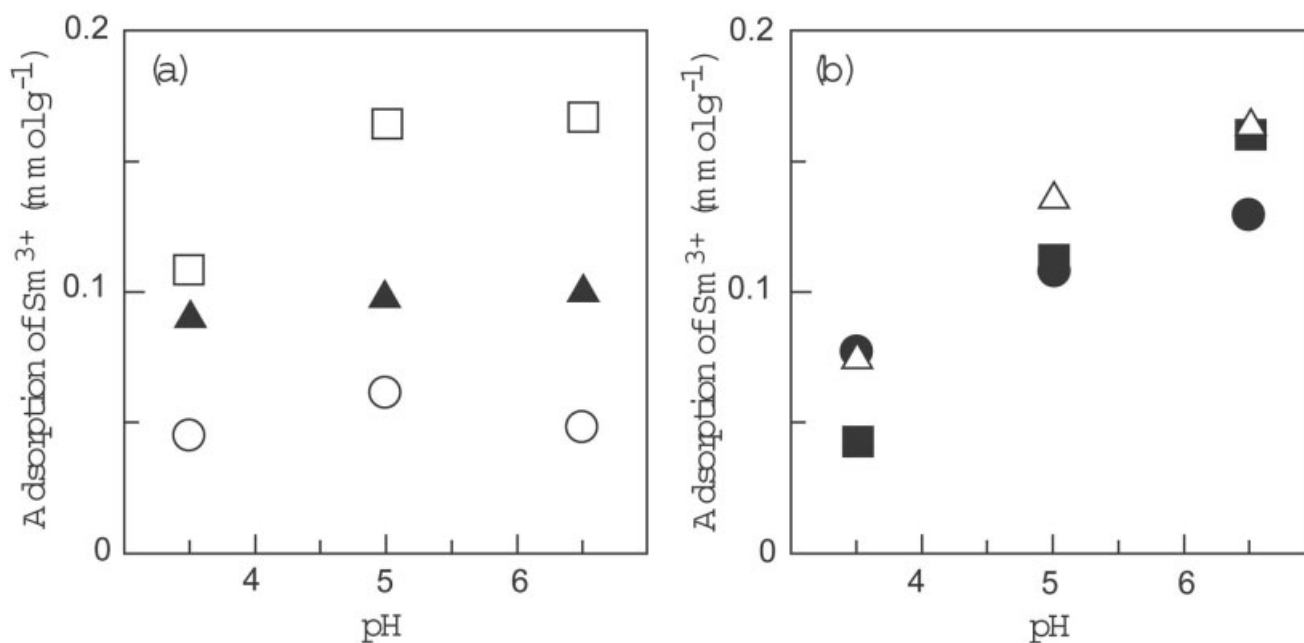


Figure 4 Adsorption of Sm^{3+} with APPO-NIPAAm-4G copolymer beads having different APPO content and different degree of crosslinking at 20°C and at various pHs. Copolymer beads: (a) APPO-NIPAAm-4G (X : 97 : 3), X-5 (○), 10 (▲), 15 (□); (b) APPO-NIPAAm-4G (X : 95 : 5), X-10 (●), 15 (△), 20 (■). Conditions: weight of gel -0.10 g; metal ion solution - 2.23×10^{-3} mol L⁻¹, 50 mL for APPO-NIPAAm-4G (X : 97 : 3); 2.68×10^{-3} mol L⁻¹, 50 mL for APPO-NIPAAm-4G (X : 95 : 5); buffer solution - $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

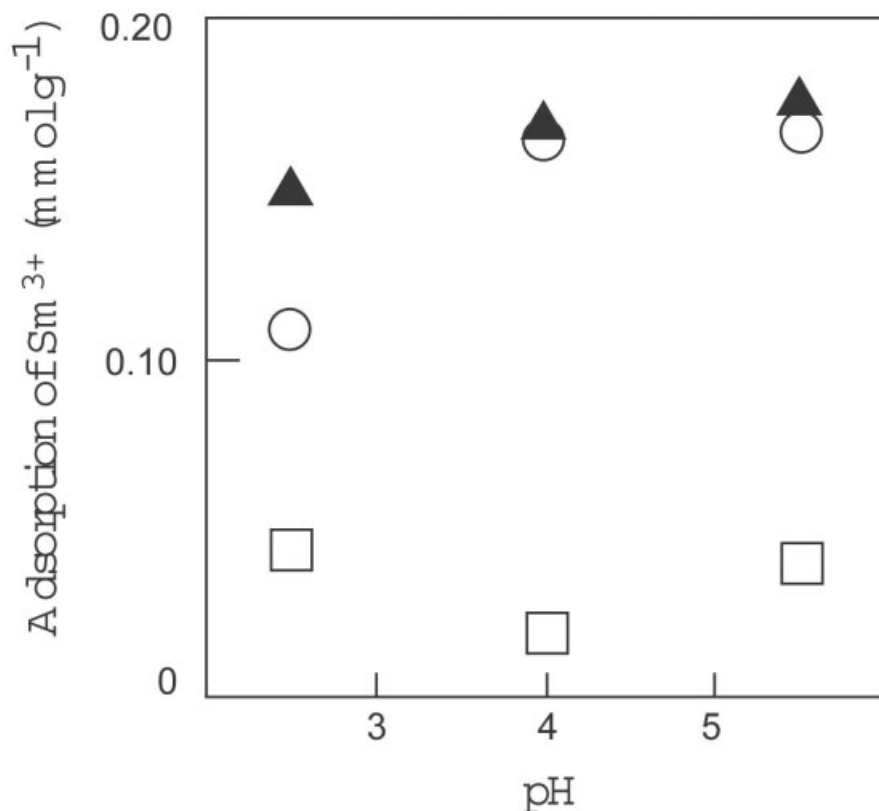


Figure 5 Adsorption of Sm^{3+} with APPO-NIPAAm-4G copolymer beads having different degree of crosslinking at 20°C and at various pHs. Copolymer beads: APPO-NIPAAm-4G (15:(100-Y):Y), Y = 3 (○), 5 (▲), 10 (□). Conditions: weight of gel = 0.10 g; metal ion solution $-2.23 \times 10^{-3} \text{ mol L}^{-1}$, 50 mL for APPO-NIPAAm-4G (X:97:3); $2.68 \times 10^{-3} \text{ mol L}^{-1}$, 50 mL for APPO-NIPAAm-4G (X:95:5); $3.25 \times 10^{-3} \text{ mol L}^{-1}$, 50 mL for APPO-NIPAAm-4G (X:90:10); buffer solution: $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

and different degree of crosslinking, for lanthanide metal ions (Eu^{3+} , Sm^{3+} , Nd^{3+} , and La^{3+}) or main transition metal ions (Cu^{2+} , Co^{2+} , and Ni^{2+}) from each single metal ion solution was measured in the pH range from 3.5 to 6.5 at 20°C .

Figures 4(a,b) show the pH dependence of the adsorption of Sm^{3+} with the APPO-NIPAAm-4G (X:97:3) (X = 5, 10, 15) and the APPO-NIPAAm-4G (X:95:5) (X = 10, 15, 20) copolymer beads, respectively. Here, X represents molar ratio of APPO in feed. In the case of the APPO-NIPAAm-4G (X:97:3) copolymer beads having low degree of crosslinking [Fig. 4(a)], the adsorption of Sm^{3+} increased with increasing APPO content in the copolymer beads and an obvious difference in the adsorption ability was observed between the copolymer beads having different APPO content. This is due to the large difference of the swelling volume of the APPO-NIPAAm-4G (X:97:3) copolymer beads having low degree of crosslinking, as shown in Figure 3(a). On the other hand, in the case of the APPO-NIPAAm-4G (X:95:5) copolymer bead having higher degree of crosslinking than the APPO-NIPAAm-4G (X:97:3) copolymer bead [Fig. 4(b)], only

a small difference in the adsorption ability was observed between the copolymer beads having different APPO content. In both APPO-NIPAAm-4G copolymer beads having different degree of crosslinking, the adsorption of metal ions increased with increasing pH of metal solutions, except for the APPO-NIPAAm-4G (5:97:3) copolymer bead. In particular, clear pH dependence on the adsorption ability was observed with the APPO-NIPAAm-4G (X:95:5) copolymer beads. The increase of the metal adsorption with increasing APPO content and increasing pH indicates that metal ions were adsorbed via coordination bond with phosphonic acid groups in the copolymer beads. The similar phenomena were also observed in the case of the adsorption of Eu^{3+} , Nd^{3+} , and La^{3+} with the APPO-NIPAAm-4G copolymer beads used for the adsorption of Sm^{3+} .

Effect of degree of crosslinking on the adsorption of metal ions with the APPO-NIPAAm-4G copolymer beads from its single metal ion solution

Next the adsorption of Sm^{3+} with the APPO-NIPAAm-4G (15:(100-Y):Y), Y = 3, 5, 10) copolymer

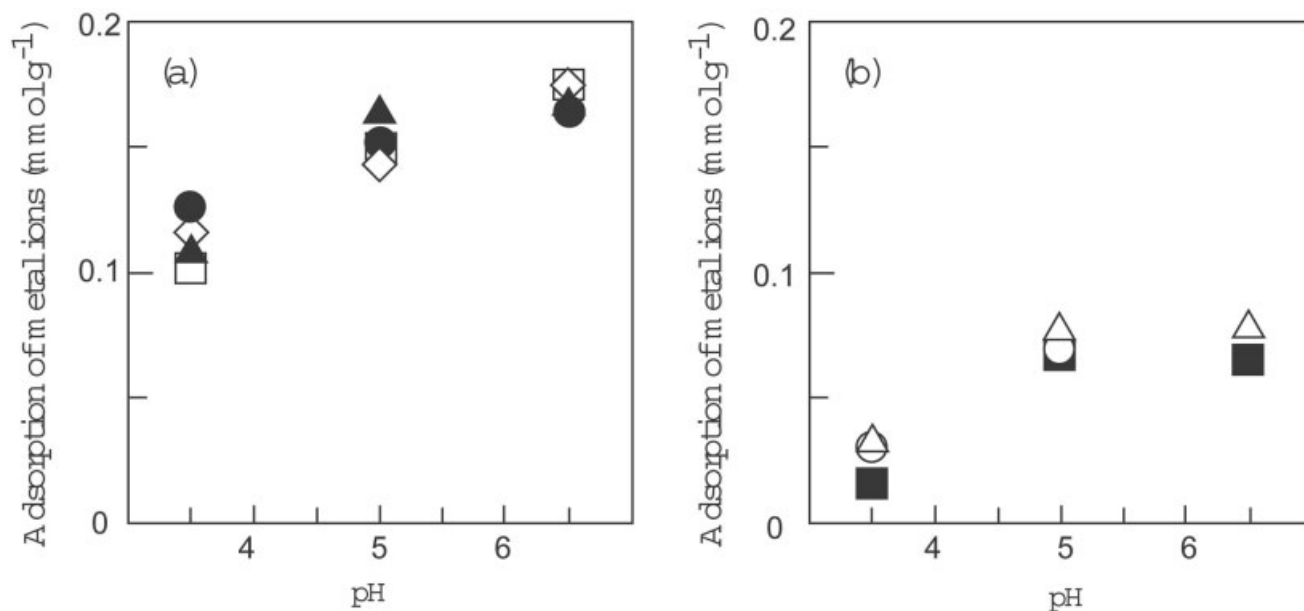


Figure 6 Adsorption of various metal ions with APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads from its single metal ion solution at 20°C and at various pHs. *Metal ions:* (a) Eu³⁺ (●), Sm³⁺ (▲), Nd³⁺ (□), La³⁺ (◇); (b) Cu²⁺ (○), Co²⁺ (△), Ni²⁺ (■); *Conditions:* weight of gel –0.10 g; metal ion solution – 2.23×10^{-3} mol L⁻¹, 50 mL; buffer solution –CH₃COOH–CH₃COONa; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

beads having different degree of crosslinking was measured at 20°C and various pHs. Here, *Y* represents the molar ratio of 4G in feed. The results are shown in Figure 5. Both the APPO-NIPAAm-4G (15 : 97 : 3) and the APPO-NIPAAm-4G (15 : 95 : 5) copolymer beads having almost the same APPO content (0.56 and 0.54 mmol/g), but different degree of crosslinking exhibited the almost the same adsorption ability for Sm³⁺ at pH 5 and pH 6.5. However, the APPO-NIPAAm-4G (15 : 90 : 10) copolymer bead having the highest degree of crosslinking had significant low adsorption ability for Sm³⁺ at every pH, although the APPO-NIPAAm-4G (15 : 90 : 10) copolymer bead had only a little bit smaller APPO content (0.47 mmol g⁻¹) than other copolymer beads. The very low metal adsorption ability of the APPO-NIPAAm-4G (15 : 90 : 10) copolymer beads with high degree of crosslinking is due to very low swelling of the copolymer bead in water at 20°C, as shown in Figure 3(c).

Adsorption of various metal ions with APPO-NIPAAm-4G (15 : 97 : 3) copolymer

Figure 6(a) shows the adsorption ability of the APPO-NIPAAm-4G (15 : 97 : 3) copolymer bead for various lanthanide metal ions (Eu³⁺, Sm³⁺, Nd³⁺, and La³⁺) from its single metal ion solution at 20°C and various pHs. The adsorption ability of the copolymer bead for each metal ion increased with increasing pH and a clear difference in the adsorption for metal ion was not observed

between each metal ion. Figure 6(b) shows the adsorption ability of the APPO-NIPAAm-4G (15 : 97 : 3) copolymer bead for various main transition metal ions (Cu²⁺, Co²⁺, and Ni²⁺) from its single metal ion solution at 20°C and at various pHs. The adsorption ability for main transition metal ions was smaller than that for lanthanide metal ions. The adsorption ability of the copolymer bead for each main transition metal ion increased also with increasing pH and a clear difference in the adsorption for main transition metal ions was not observed between each metal ion.

Adsorption of metal ions with the APPO-NIPAAm-4G copolymer beads from mixed metal ion solutions

As mentioned earlier, the APPO-NIPAAm-4G copolymer beads exhibited higher adsorption ability for lanthanide metal ions than for main transition metal ions. Figure 7 shows the selective adsorption of Eu³⁺ against Cu²⁺ from their mixed (Eu³⁺/Cu²⁺ = 1/1 molar ratio) solutions at pH 3.5, 5.0, and 6.5. At pH 3.5 and pH 5.0, only Eu³⁺ was almost adsorbed with the copolymer bead, while at pH 6.5, about three times Eu³⁺ to Cu²⁺ was adsorbed with the copolymer bead from their mixed solution. Thus, the APPO-NIPAAm-4G copolymer beads were found to have high selective adsorption of lanthanide metal ions against main transition metal ions from their mixed solution.

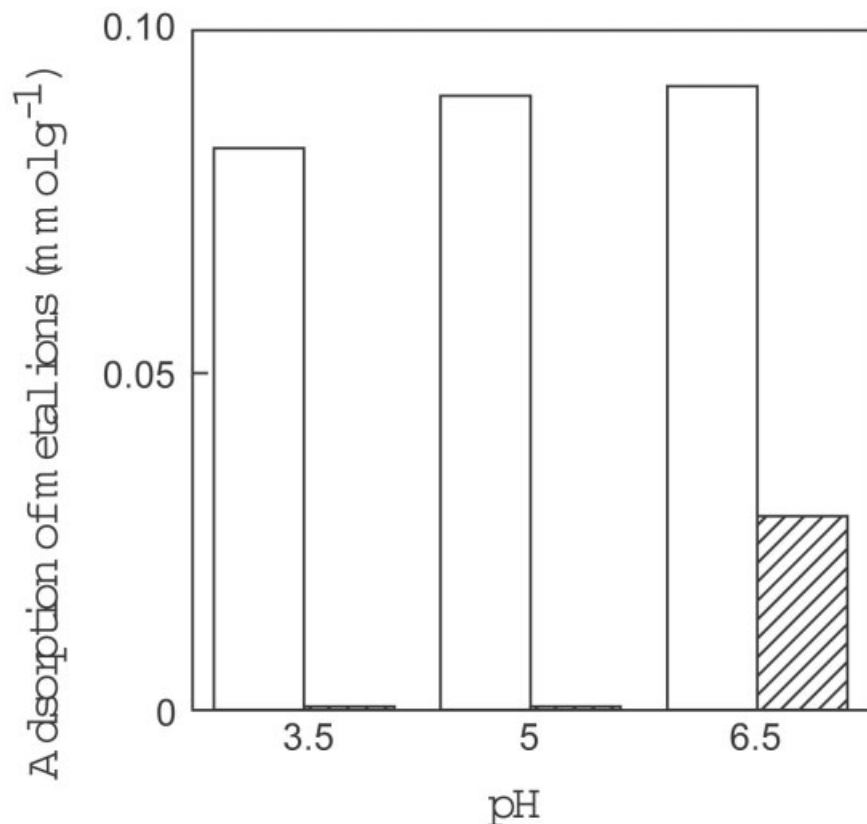


Figure 7 Adsorption of metal ions (Eu^{3+} , Cu^{2+}) with APPO-NIPAAm-4G (15:97:3) copolymer beads from mixed metal ion solutions of different pH. *Metal ions:* Eu^{3+} (\square), Cu^{2+} (hatched) *Conditions:* weight of gel -0.10 g; each metal ion solution -2.23×10^{-3} mol L^{-1} , 50 mL; buffer solution $-\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

Figure 8 shows the selective adsorption between lanthanide metal ions ($\text{Eu}^{3+}/\text{Sm}^{3+}$, $\text{Sm}^{3+}/\text{Nd}^{3+}$, and $\text{Nd}^{3+}/\text{La}^{3+}$) from their mixed (1/1 molar ratio) solutions at pH 3.5, 5.0, and 6.5. The APPO-NIPAAm-4G copolymer beads had higher adsorption ability for

Eu^{3+} than Sm^{3+} , Sm^{3+} than Nd^{3+} , and Nd^{3+} than La^{3+} from their mixed solutions, although a clear difference in the metal adsorption was not observed with the copolymer bead from its single metal ion, as shown in Figure 6. Accordingly, the order of adsorp-

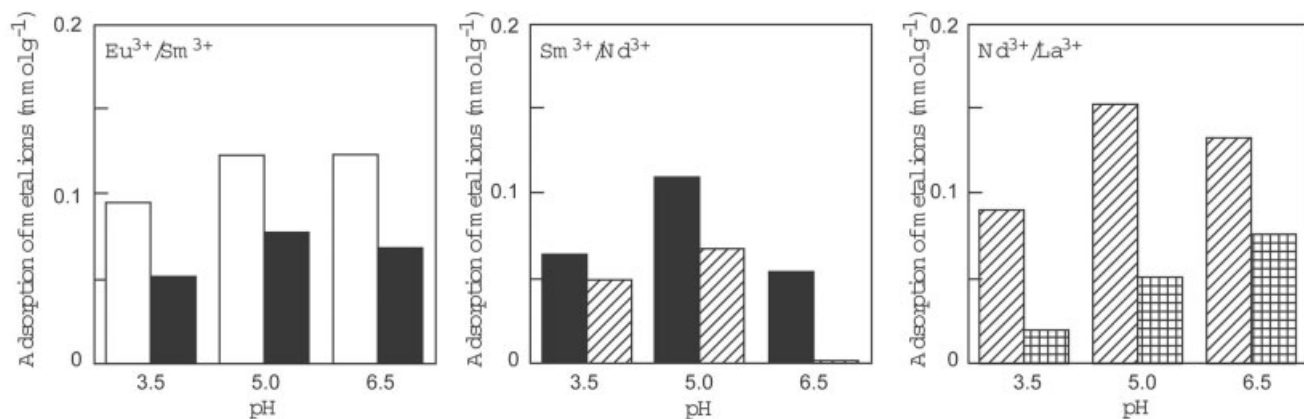


Figure 8 Adsorption of lanthanide metal ions with APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads from mixed metal ion solutions of different pH. *Metal ions:* Eu^{3+} (\square), Sm^{3+} (\blacksquare), Nd^{3+} (hatched), La^{3+} (grid). *Conditions:* weight of gel -0.10 g; each metal ion solution -2.23×10^{-3} mol L^{-1} , 50 mL; buffer solution $-\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

TABLE III
Selectivity Coefficient (K) of Adsorption for $M_1^{3+}/M_2^{3+a,b}$

Metal ion solution M_1^{3+}/M_2^{3+}	Temperature (°C)	Concentration ratio in solution $[M_1^{3+}]/[M_2^{3+}]$	Selectivity coefficient (K)		
			pH 3.5	pH 5.0	pH 6.5
Eu^{3+}/Si^{3+}	20	1/1	1.83	1.58	1.82
Sm^{3+}/Nd^{3+}	20	1/1	1.31	1.63	8.43
Nd^{3+}/La^{3+}	20	1/1	4.49	3.01	1.75
Sm^{3+}/Nd^{3+}	10	1/1	2.88	2.52	2.83
	20	1/1	1.31	1.63	8.43
	30	1/1	3.53	2.52	1.17
Eu^{3+}/La^{3+}	20	4/1	—	—	4.64
	20	2/1	—	—	2.30
	20	1/2	—	—	4.18
	20	1/4	—	—	9.97

^a Selectivity coefficient (K) = (M_1^{3+}/M_2^{3+} molar ratio adsorbed with the copolymer beads)/(M_1^{3+}/M_2^{3+} molar ratio in the solution).

^b Selectivity coefficients of adsorption from each mixed metal ion solution were calculated from the data in Figures 8–10 (indicated as three groups within the body of the table).

tion ability of the APPO-NIPAAm-4G copolymer beads for lanthanide metal ions was as follows: $Eu^{3+} > Sm^{3+} > Nd^{3+} > La^{3+}$

This order is in accordance with the order of the magnitude of atomic number of these metal ions. It is known that lanthanide metal ion with larger atomic number has lower ion radius than that with small atomic number, because, in lanthanide metal series, inner shell is faster filled with electron than the outer shell.²¹ Therefore, this indicates that metal ion with larger atomic number has higher ion density on its surface than that with smaller atomic number. This is due to the order in the adsorption of lanthanide metal ions ($Eu^{3+} > Sm^{3+} > Nd^{3+} > La^{3+}$). The selectivity coefficient of adsorption for mixed metal ion (Eu^{3+}/Sm^{3+} , Sm^{3+}/Nd^{3+} , and Nd^{3+}/La^{3+}) is listed in Table III. The selectivity coefficient (K) was calculated by using eq. (2).

$$\text{Selectivity coefficient } (K) = \frac{(M_1^{3+}/M_2^{3+} \text{ molar ratio adsorbed with the copolymer beads})}{(M_1^{3+}/M_2^{3+} \text{ molar ratio in solutions})} \quad (2)$$

Clear pH dependence of the selectivity coefficient for each mixed metal ion was not observed such as in the case of Eu^{3+}/Cu^{2+} .

We previously mentioned that the swelling volume of the APPO-NIPAAm-4G copolymer beads decreased with increasing temperature. Therefore, the selective adsorption between Sm^{3+} and Nd^{3+} with the APPO-NIPAAm-4G (15 : 97 : 3) copolymer bead was measured at various temperatures (10, 20, and 40°C) at different pHs (3.5, 5.0, and 6.5). The results are shown in Figure 9. At every temperature, Sm^{3+} was adsorbed more than Nd^{3+} with the copolymer beads. The adsorption of metal ions at 40°C was fairly low com-

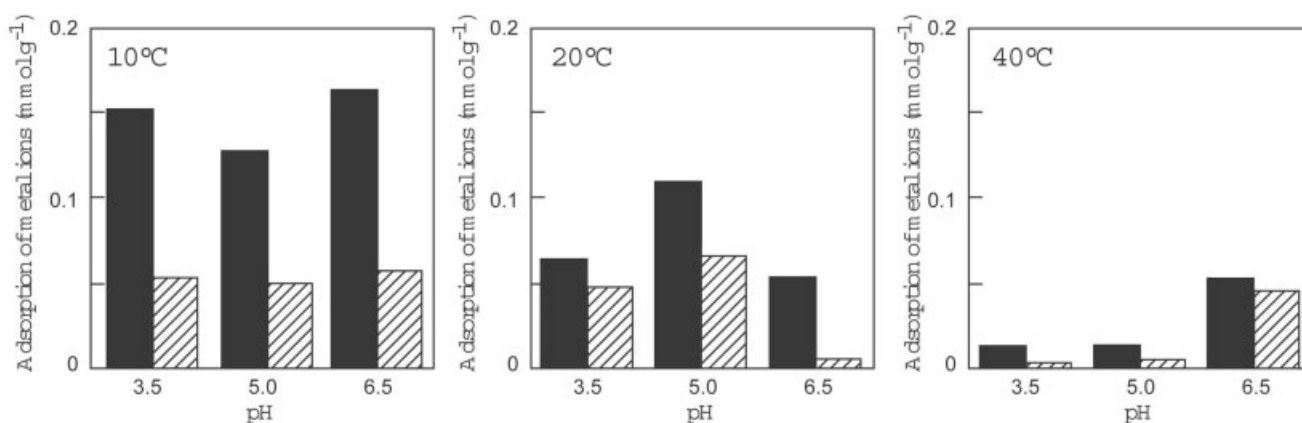


Figure 9 Adsorption of metal ions (Sm^{3+} , Nd^{3+}) with APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads from mixed metal ion solutions of different pH at various temperatures. Metal ions: Sm^{3+} (■), Nd^{3+} (▨). Conditions: weight of gel –0.10 g; each metal ion solution $-2.23 \times 10^{-3} \text{ mol L}^{-1}$, 50 mL; buffer solution $-\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$.

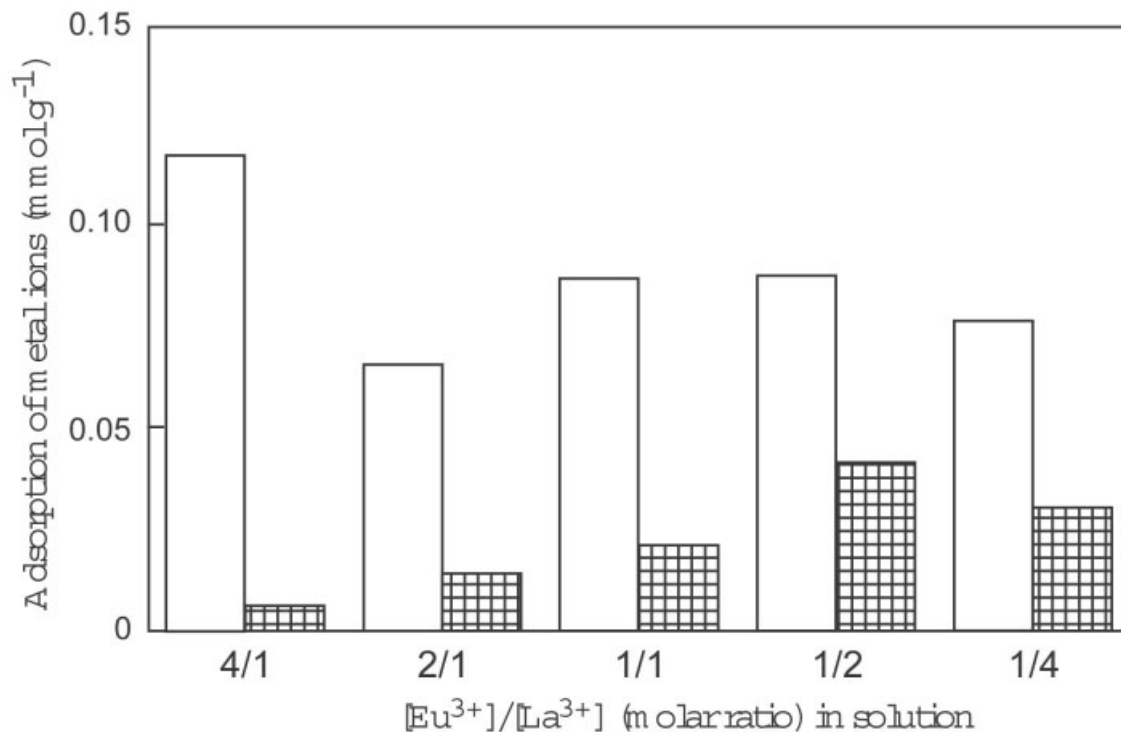


Figure 10 Adsorption of metal ions (Eu^{3+} , La^{3+}) with APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads from mixed metal ion solutions with various concentration ratios. *Metal ions:* Eu^{3+} (\square), La^{3+} (\boxplus). *Conditions:* weight of gel = 0.10 g; metal ion solution = $2.23 \times 10^{-3} \text{ mol L}^{-1}$, 50 mL; added metal ions/phosphinic acid in copolymer (molar ratio) = 2/1; buffer solution (pH = 6.5) = $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; shaking at 20°C for 24 h; swelling at 20°C for 24 h.

pared with that at 10°C and 20°C . This is due to the lower swelling of the copolymer beads at 40°C than at 10°C and 20°C . The selectivity coefficient of adsorption for mixed metal ion ($\text{Sm}^{3+}/\text{Nd}^{3+}$) is also listed in Table III. Neither temperature dependence nor pH dependence of the selectivity coefficient of the adsorption of $\text{Sm}^{3+}/\text{Nd}^{3+}$ could obviously be observed.

To ascertain high selective adsorption of Eu^{3+} against La^{3+} , the adsorption of these metal ions was measured from mixed solutions with different composition ($\text{Eu}^{3+}/\text{La}^{3+} = 4/1-1/4$ molar ratio) at 20°C and at pH 6.5 (buffer solution). The results are shown in Figure 10. It was found that Eu^{3+} was adsorbed more highly than La^{3+} , even from mixed solutions ($\text{Eu}^{3+}/\text{La}^{3+} = 1/2$ and $1/4$ molar ratio) having smaller content of Eu^{3+} than La^{3+} . The selectivity coefficient of adsorption for $\text{Eu}^{3+}/\text{La}^{3+}$ is also listed in Table III. The highest selectivity coefficient of $\text{Eu}^{3+}/\text{La}^{3+}$ was obtained from mixed solution ($\text{Eu}^{3+}/\text{La}^{3+} = 1/4$ molar ratio). Thus, it was found that the APPO-NIPAAm-4G copolymer beads exhibited very high selective adsorption of Eu^{3+} against La^{3+} .

To ascertain this higher selective adsorption of Eu^{3+} against La^{3+} , the substitution adsorption of Eu^{3+} and La^{3+} with the APPO-NIPAAm-4G (15 : 97 : 3) copolymer bead was measured by a batch method at 20°C and at pH 6.5 (buffer solution). The results are shown

in Figure 11. First, Eu^{3+} was adsorbed with the copolymer beads and the copolymer beads were washed with deionized water, and then La^{3+} was adsorbed with same copolymer beads. Figure 11(a) shows that a part of Eu^{3+} adsorbed first with the copolymer beads was substituted with La^{3+} . On the other hand, Figure 11(b) shows that La^{3+} adsorbed first with the copolymer beads was substituted with more Eu^{3+} . This result indicates that the APPO-NIPAAm-4G copolymer beads had higher adsorption ability for Eu^{3+} than La^{3+} .

Adsorption of metal ions by column method

The adsorption of Eu^{3+} and La^{3+} with the APPO-NIPAAm-4G (15 : 97 : 3) copolymer bead was carried out by a column method, from their mixed solution ($\text{Eu}^{3+}/\text{La}^{3+} = 1/1$ molar ratio) at 25°C . The results are shown in Figure 12(a). La^{3+} was adsorbed completely until 10 bed volumes, and then the concentration of La^{3+} in effluent increased rapidly, while Eu^{3+} was adsorbed completely until 45 bed volumes, and then the concentration of Eu^{3+} increased gradually. The concentration of La^{3+} in effluent above 35 bed volumes became more than 0.25 mmol L^{-1} of its initial concentration. This is due to the fact that La^{3+} ad-

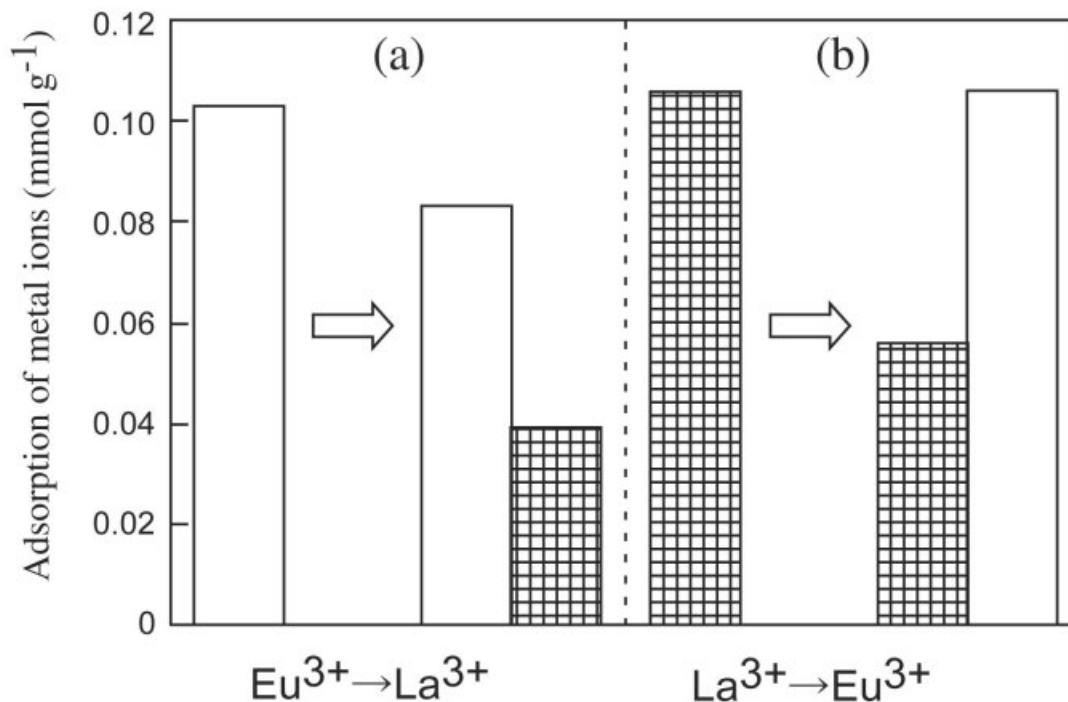


Figure 11 Substitution adsorption of metal ions adsorbed on APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads. *Metal ions:* Eu^{3+} (\square), La^{3+} (\boxplus). *Conditions:* weight of gel -0.10 g; metal ion solution -1.13×10^{-3} mol L^{-1} , 50 mL; added metal ions/phosphinic acid in copolymer (molar ratio) = 1/1; buffer solution (pH = 6.5) $-\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$; swelling at 20°C for 24 h; shaking at 20°C for 24 h.

sorbed first on the copolymer beads was substituted with Eu^{3+} . After adsorption of metal ions, the copolymer beads was washed with deionized water until no

metal ions was detected, and then the elution of metal ions from the copolymer beads was carried out by passing 1 mol L^{-1} HCl solution through the column.

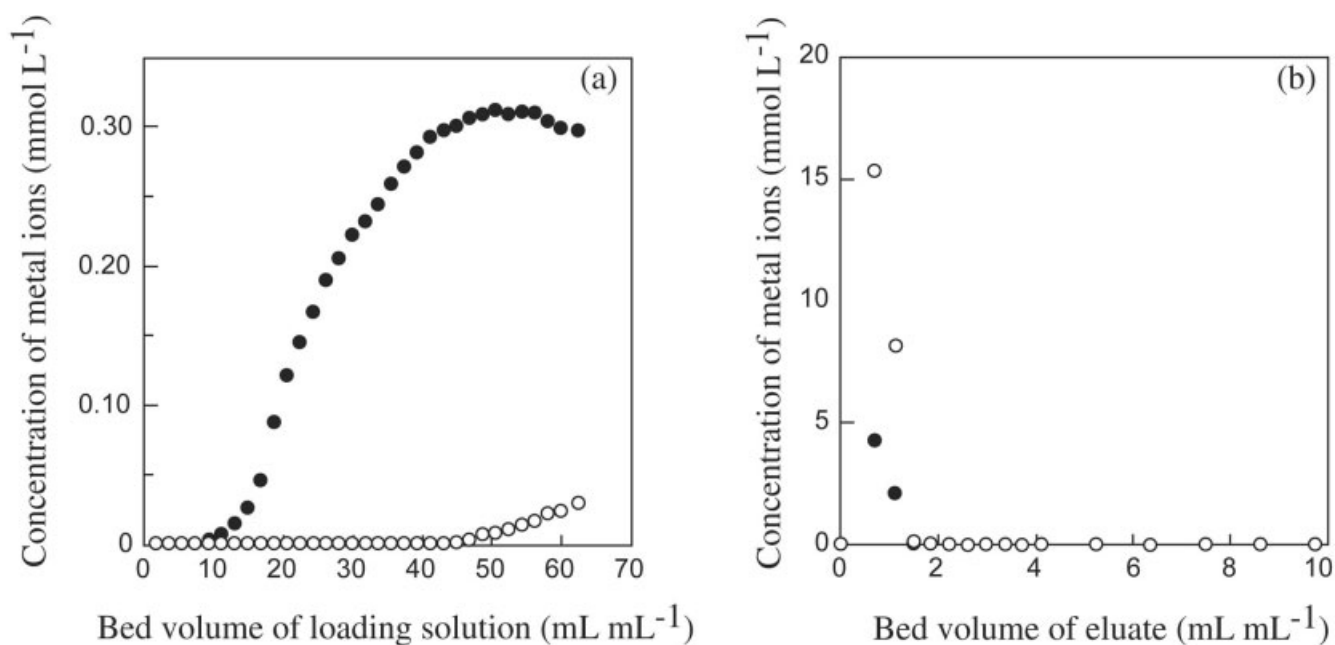


Figure 12 Adsorption (a) and desorption (b) of metal ions with APPO-NIPAAm-4G (15 : 97 : 3) copolymer beads from mixed metal ion solution by column method. *Metal ions:* Eu^{3+} (\circ), La^{3+} (\bullet). *Conditions:* weight of gel -2.0 g; column diameter -1.0 mL; resin bed volume -8.0 mL; eluate -1 mol L^{-1} HCl; flow rate -1.0 mL min^{-1} ; temperature -25°C ; (a) load metal ion solution -0.5 mmol L^{-1} ; (b) eluate: 1 mol L^{-1} HCl.

The results are shown in Figure 12(b). Both metal ions were easily eluted with 1 mol L⁻¹ HCl solution until two bed volumes. From the adsorption and elution data, the elution percentage of Eu³⁺ and La³⁺ were 77.2% and 74.9%, respectively. To get higher elution percent of metal ions, the concentration of HCl should be increased. Thus, high selective adsorption for Eu³⁺ than La³⁺ with the APPO-NIPAAm-4G copolymer beads was also observed by a column method.

CONCLUSIONS

1. The APPO-NIPAAm-4G copolymer beads were obtained in a good yield by suspension copolymerization of monomers (APPO, NIPAAm, and 4G) dissolved in chloroform, in a saturated Na₂SO₄ aqueous solution in the presence of surfactant and MgCO₃.
2. The APPO-NIPAAm-4G copolymer beads had higher adsorption capacity for lanthanide metal ions (Eu³⁺, Sm³⁺, Nd³⁺, or La³⁺) than for main transition metal ions (Cu²⁺, Ni²⁺, or Co²⁺).
3. The APPO-NIPAAm-4G copolymer beads had selective adsorption ability for lanthanide metal ions in the following order: Eu³⁺ > Sm³⁺ > Nd³⁺ > La³⁺.
4. The high selective adsorption between lanthanide metal ions was observed from their mixed metal ion solutions by both a batch method and a column method.

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