



Thermosensitive gels incorporating polythioether units for the selective extraction of class *b* metal ions

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ARTICLE INFO

Article history:

Available online 16 July 2010

Keywords:

Poly-N-isopropylacrylamide
Pre-concentration
Silver ion
Copper(I) ion
Palladium ion
9-Aza-3,6,12,15-tetrathiaheptadecane
Extraction
Lower critical solution temperature

ABSTRACT

Novel temperature-responsive copolymers of N-isopropylacrylamide and monoaza-tetrathioether derivative, were synthesized for the selective extraction of soft metal ions such as silver(I), copper(I), gold(III) and palladium(II) ion. The ratio between N-isopropylacrylamide group and monoaza-tetrathioether group in the copolymer was determined. The ratio between N-isopropylacrylamide group and monoaza-tetrathioether group varied in the range of 66:1–187:1. Each lower critical solution temperature (LCST) of the polymer solution was determined spectrophotometrically by the relative absorbance change at 750 nm via temperature of the polymer solution. Metal ion extraction using the copolymer with appropriate counter anions such as picrate ion, nitrate or perchlorate ion was examined. Soft metal ions such as silver(I), copper(I), gold(III) and palladium(II) ion were extracted selectively into the solid polymer phase. The extraction efficiency of a metal ion such as silver ion increased as the increase of the ratio of the monoaza-tetrathioether group to N-isopropylacrylamide group in the polymer. The quantitative extraction of class *b* metal ions as well as the liquid–liquid extraction of metal ions with monoaza-tetrathioether molecule was performed.

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1. Introduction

The studies of poly-N-isopropylacrylamide for separation science have been developed since 1990s, because of its temperature responsive character [1–3]. It has a lower critical solution temperature (LCST) and the polymer is soluble in water below the LCST, then the insoluble polymer phase of small volume formed as the solution temperature increased above the LCST [1–3]. Some hydrophobic species move into the solid phase formed. Therefore, this polymer formed extracts with a variety of compounds such as ion-paired complexes of metal ions, aromatic hydrocarbons and some environmental endocrine disruptors such as alkylphenols and phthalic esters [4]. It may make the separation and pre-concentration of hydrophobic species possible. A part of chromatographic studies emphasize that the poly-N-isopropylacrylamide immobilized silica introduce the separation which controlled by temperature or salt concentration [5–7]. However, the pre-concentration and separation of hydrophobic species have been achieved, such extraction methods were not selective for any chemical species. Therefore, the combination of poly-N-isopropylacrylamide and a selective extractant may change such thermoresponsive polymer extraction. Takeshita et al. exam-

ined the separation of Americium(III) and Europium(III) using the copolymer of N-isopropylacrylamide and N-donor atom containing ligand [8–10]. On the other hand, thioether chemistry has been developed since 1970 [11–18]. Macrocyclic polythioethers (thiacrownethers) are known as highly selective soft metal extractants [13,14]. Acyclic analogues of thiocrownethers also react selectively with soft metal ions such as silver, copper(I), mercury and palladium ions, because the thioether group has a softer Lewis basis than the mercapto group [14–17]. The author examined the extraction behavior of the ion pair of silver-trithioether derivative complexes with picrate ion into polymer phase of poly-N-isopropylacrylamide [20]. The results indicated the possibility of the pre-concentration of silver ion with thioether-containing ligand and counter anion into poly-N-isopropylacrylamide as extraction media. In this study, temperature responsive copolymers of N-isopropylacrylamide and monoaza-tetrathioether derivative, 9-acryloyl-9-aza-3,6,12,15-tetrathiaheptadecane (ATH) as shown in Fig. 1, were synthesized for the extraction of soft metal ions such as silver(I), copper(I), gold(III) and palladium(II) ion. The ratio between N-isopropylacrylamide group and ATH group in the copolymer was determined by measuring the sulfur atom emission with ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) to determine the sulfur atom concentration in the polymer solution. It would be possible to investigate the relationship between the change of the ratio of ATH vs. N-isopropylacrylamide and the property change of the polymer. It was impossible to determine the ratio of N-donor ligand in the polymer [8–10]. Each lower critical solution temperature (LCST) of

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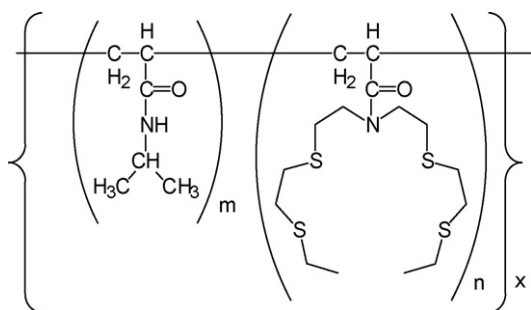


Fig. 1. Structure of ATH-NIPAAm copolymer.

the polymer solution was determined spectrophotometrically by the relative absorbance change at 750 nm via temperature of the polymer solution. Metal ion extraction using the copolymer with appropriate counter anions such as picrate, nitrate or perchlorate ion was examined.

2. Experimental

2.1. Apparatus

^1H NMR spectra were recorded on a Varian UNITY300. Spectra were measured in CDCl_3 . Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) Vista MPX (Seiko Instruments, Japan) was used for the determination of the sulfur atoms in the copolymer synthesized. Gel permeation chromatography system (Shodex, Japan) was used for measuring the molecular weight of the copolymer synthesized. An UV-visible spectrophotometer U-3310 (Hitachi, Japan) was used for measuring the LCST. The metal ion concentrations were determined by a Z-5310 (Hitachi, Japan) atomic absorption spectrometer. The pH of aqueous solution was measured by a M-12 pH meter (Horiba, Japan).

2.2. Synthesis

2.2.1. Reagents

Reagents used for synthesis and analysis, were guaranteed ones. Hydrochloric acid and sulfuric acid (Wako pure chemical, Japan)

were of analytical grade. A part of N-isopropylacrylamide (NIPAAm) was provided from Kojin Co., Japan.

2.2.2. Synthesis of 9-acryloyl-9-aza-3,6,12,15-tetrathiaheptadecane (acryloyl-ATH)

The monomer unit 9-acryloyl-9-aza-3,6,12,15-tetrathiaheptadecane was synthesized by the following reaction. The reagent containing thioether unit, 9-aza-3,6,12,15-tetrathiaheptadecane (ATH) was synthesized by the reaction between bis(2-chloroethyl)amine hydrochloride and ethylthioethanethiol in alkaline solution as described before [19]. The ATH-hydrochloride (3.3 g) was added into 80 ml of 1 M NaOH solution and stirred in the 300 ml round bottom flask. Neutralized ATH was extracted into dichloromethane and dried over sodium sulfate. After the filtration, sodium carbonate (15.4 g) and acryloyl chloride were added into the dichloromethane solution, and stirred over night at room temperature. The residue, after the solvent was evaporated in vacuo, was purified with column chromatography (hexane:ethylacetate = 1:9). The desired product was obtained in a 79.7% yield. Reagents synthesized were isolated by NMR spectra.

^1H NMR (CDCl_3 , delta, ppm): 1.23–1.30 (m, 6H, CH_3), 2.53–2.62 (m, 4H, CH_2CH_2), 2.78–2.84 (m, 8H, CH_2CH_2), 2.70–2.76 (m, 4H, SCH_2CH_2), 3.55–3.60 (t, 4H, CH_2N), 5.69–5.73 (d, 1H, CH), 6.31–6.37 (d, 1H, CH), 6.48–6.57 (q, 1H, CHCO).

2.2.3. Synthesis of ATH-NIPAAm copolymer

The synthetic routes for ATH-NIPAAm copolymer are shown in Fig. 2. Into 4 ml of N,N-dimethylformamide as a solvent, α,α' -azobisisobutyronitrile as the initiator and two monomers (NIPAAm and acryloyl-ATH) were added. The resulting solution was degassed with nitrogen for about 15 min. The molar ratio of N-isopropylacrylamide and 9-acryloyl-ATH was varied in a range between 20:1 and 150:1 in feed. The polymer synthesized (ATH-NIPAAm) was dissolved in an aliquot volume of water. The gels were washed with double distilled water and kept in water for 4–6 days for the removal of the unreacted monomers and then evaporated. The number average molecular weight and the weight average molecular weight were measured with the gel permeation chromatography. Then, the degree of dispersion was estimated for each ATH-NIPAAm copolymer. The sulfur atom concentration of the solution was determined by ICP-AES. The emission line

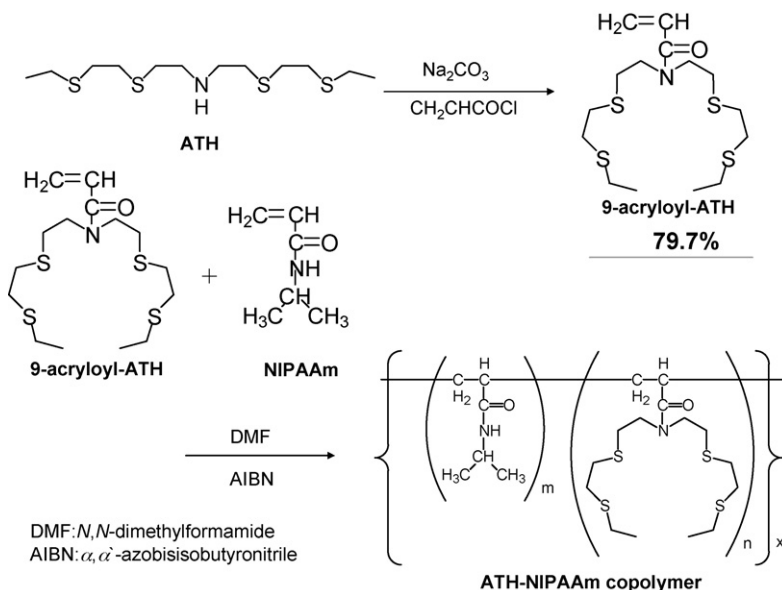


Fig. 2. Synthetic route of ATH-NIPAAm copolymer.

181.972 nm was used for the detection of sulfur atom emission. The standard solution was prepared with sodium sulfate with the range of 0.00–6.00 ppm.

2.3. LCST

The lower critical solution temperature (LCST) was determined spectrophotometrically using a Hitachi U-3200 spectrophotometer by the relative absorbance change at 750 nm via temperature of the solution. The ATH–NIPAAm copolymer was dissolved below the room temperature. The ion strength of the solution of 0.025% (w/v) ATH–NIPAAm copolymer was kept at 0.1 with sodium sulfate. Transmittance of the solution at various temperatures was measured.

2.4. Extraction of metal ions

2.4.1. Metal ion extraction with the ATH–NIPAAm copolymer

An aliquot of aqueous solution containing 2.5×10^{-5} M metal ion, 3.3×10^{-2} M sodium sulfate, 1×10^{-3} M counter anions such as nitrate, perchlorate or picrate ion, 1×10^{-2} M buffer solution and 0.025% (w/v) ATH–NIPAAm copolymer in a stoppered cylindrical tube was shaken at 25 °C for 10 min and then 70 °C for 20 min. After the polymer phase was separated, the metal ion concentrations in aqueous phase and in the solution in which the polymer phase dissolved in 0.1 M nitric acid, were determined by an atomic absorption spectrometer. The pH of aqueous phase was measured. The buffer solutions, sulfuric acid for pH 1–3, acetate–acetic acid for pH 4–6, borax–boric acid for pH 7–9 and borax–sodium hydroxide for pH 10–12 were used. The reducing agent for the Cu(I) and Fe(II), 3.3×10^{-2} M hydroxyl-ammonium sulfate was used.

2.4.2. Liquid–liquid extraction of metal ions

An aliquot of aqueous solution (10 ml) containing 2.5×10^{-5} M metal ion, 3.3×10^{-2} M sodium sulfate, 1×10^{-3} M counter anions such as nitrate, perchlorate or picrate ion, 1×10^{-2} M buffer solution and 10 ml of 1,2-dichloroethane solution of ATH in a stoppered cylindrical tube was shaken at 25 °C for 30 min. After two phases were separated, the metal ion concentrations in aqueous phase and organic phase in which the solvent was evaporated and the residue was decomposed with concentrated nitric acid and diluted with water, were determined by an atomic absorption spectrometer. The pH of aqueous phase was measured [14].

3. Results and discussion

3.1. Synthesis of the copolymer

In this study, monoaza-tetrathioether ligand ATH was used as the extraction unit in the copolymer. Some copolymers of various ratios of ATH to NIPAAm were synthesized successfully. In several studies, researchers used the combination of NIPAAm and ligands which contained N-donor atoms or O-donor atoms [8–10]. In such cases, it was difficult to determine the ratio of NIPAAm and those ligands, because the NIPAAm unit itself has N and O atoms. As shown in Table 1, it was possible to determine the ratio of

Table 1

The determination of the ratio of ATH to NIPAAm in the polymer.

ATH:NIPAAm (in feed)	Sulfur in ATH–NIPAAm copolymer (ppm)	ATH:NIPAAm (determined)
1:50	8.23	1:66
1:70	6.50	1:84
1:100	3.98	1:139
1:150	2.98	1:187
PNIPAAm (purchased)	0	0:1

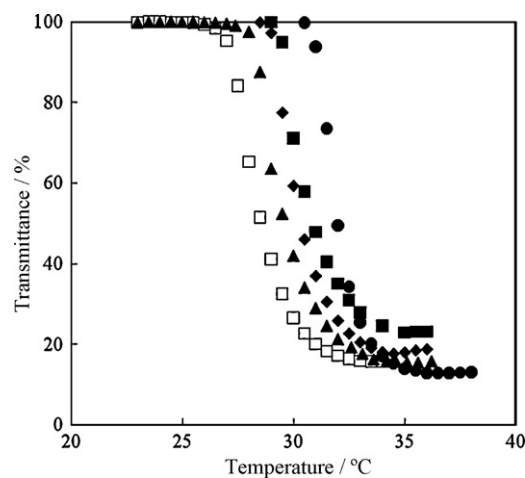


Fig. 3. Plots of transmittance of 750 nm vs. temperature. Concentration of ATH–NIPAAm 0.025%, w/v; Na₂SO₄, 3.3×10^{-2} M; □, 1:66; ▲, 1:84; ◆, 1:139; ■, 1:187; ●, PNIPAAm.

ATH to NIPAAm, by measuring the sulfur atom emission intensity with ICP–AES. The ratio was found as 1:31, 1:66, 1:84, 1:139 and 1:187. After the synthesis of the copolymer, the determined ratio of ATH/NIPAAm slightly decreased than that of feed. Table 2 shows the number average molecular weight (Mn), the weight average molecular weight (Mw) and the ratio (Mw/Mn) which shows the degree of dispersion for each ATH–NIPAAm copolymer. The number average molecular weight for synthesized copolymer was above 10,000, and not so different from that of PNIPAAm purchased. The increase of the ratio of ATH to NIPAAm did not insist on the change of degree of dispersion. In this study, the copolymer showed different physical properties depending on the mole fraction of ATH unit.

3.2. LCST

Behavior of the phase transfer of the copolymer in the solution, depending on the temperature, was examined. Then the lower critical solution temperature (LCST) was estimated spectrophotometrically. Fig. 3 shows the plots of the transmittance at 750 nm of the copolymer solution vs. the temperature of the copolymer solution. The LCST of ATH–NIPAAm copolymer (1:187) was 34.5 °C, almost the same as that of poly-N-isopropylacrylamide (PNIPAAm). Therefore, the ATH–NIPAAm copolymer showed phase transition

Table 2

Average molecular weight of ATH–NIPAAm copolymer.

ATH:NIPAAm (determined)	Number average molecular weight (Mn)	Weight average molecular weight (Mw)	Degree of dispersion (Mw/Mn)
1:66	11000 ± 3000	56000 ± 11000	5.1
1:84	12000 ± 5000	81000 ± 22000	6.8
1:139	14000 ± 3000	32000 ± 1000	2.3
1:187	10000 ± 4000	86000 ± 21000	8.6
PNIPAAm (purchased)	16000 ± 3000	29000 ± 1000	1.8

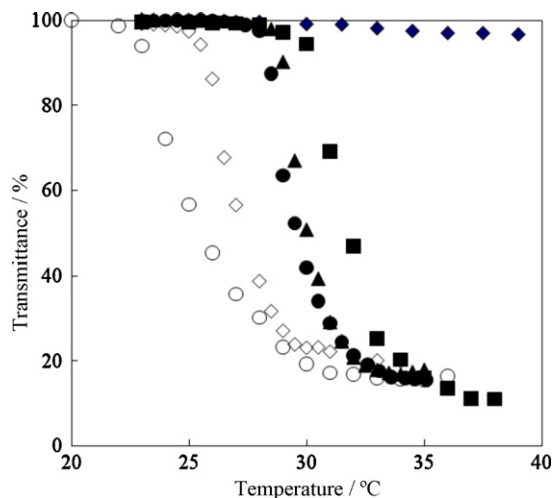


Fig. 4. Plots of transmittance at 750 nm vs. temperature of the ATH-NIPAAm solution. Concentration of ATH-NIPAAm (1:84); 0.025%, w/v. Concentration of Na₂SO₄ ♦, 0 M; ■, 3.3×10^{-3} M; ▲, 1.7×10^{-2} M; ●, 3.3×10^{-2} M; ◇, 6.6×10^{-2} M; ○, 0.1 M.

phenomena, in which the copolymer was swollen at below 34.5 °C and shrunken at the temperature higher than the LCST. The result indicates the possibility of the pre-concentration or extraction of metal ions as well as the use of the combination of poly-NIPAAm and ATH described before [20]. The LCST was estimated from the curve of the plots for each copolymer of various ratios. The results indicate that the LCST decreased as the mol fraction of ATH in the copolymer increased. As the ATH unit containing the thioether groups has a hydrophobic character, it may accelerate the dehydration of the copolymer and shift the LCST lower than that of pure poly-PNIPAAm. Fig. 4 shows the effect of salt concentration on the LCST in the copolymer solution. Sodium sulfate and the copolymer ATH-NIPAAm (1:84) were used. When sodium sulfate was absent in the solution, LCST disappeared. The phase transfer accompanied dehydration might be facilitated by the effect of salting out. The results indicate that the increase of salt concentration caused the decrease of LCST.

When the extraction of the metal ion by the ATH-NIPAAm copolymer is performed, the co-extracted counter anions might be in the solution. It will affect the phase transfer phenomena. Counter anions such as nitrate, perchlorate and picrate ions were used for the liquid-liquid extraction of metal ions with thioether derivatives. Fig. 5 shows the plots of the transmittance at 750 nm of the

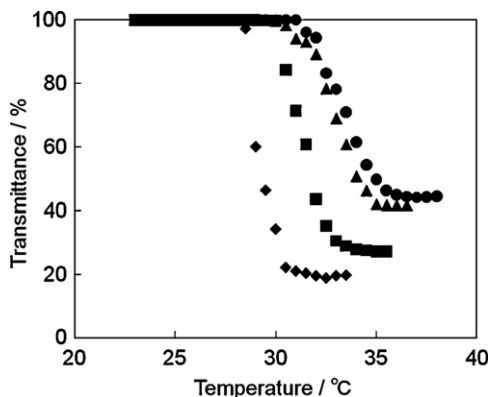


Fig. 5. Plots of transmittance vs. temperature of the ATH-NIPAAm solution. Measurement wavelength of 750 nm, concentration of ATH-NIPAAm (1:84), 0.025%, w/v; Ag(I) ion, 2.5×10^{-5} M; Na₂SO₄, 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; counter anion, 1.0×10^{-3} M; pH, 4; counter anions: ♦, picrate ion; ■, perchlorate ion; ▲, nitrate ion; ●, none.

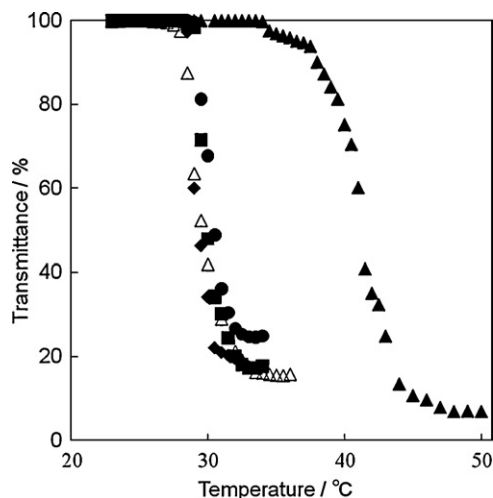


Fig. 6. Plots of transmittance vs. temperature. Measurement wavelength of 750 nm, concentration of ATH-NIPAAm (1:84) 0.025%, w/v; metal ion, 2.5×10^{-5} M; picric acid, 1.0×10^{-3} M; Na₂SO₄, 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; NH₂OH, 3.3×10^{-2} M for Cu(I) ion; pH, 4–5; metal ions: ♦, silver(I) ion; ■, copper(I) ion; ▲, palladium(II) ion; ●, aurate(III) ion; △, none.

copolymer solution vs. the temperature of the solution in which silver ion and a counter anion were added. The curve shifted to the lower temperature with the order of picrate < perchlorate < nitrate ion ~ none ("none" means, no addition of counter anion with the exception of the anions which are included in the buffer solution). This order is the same as that of the liquid-liquid extraction efficiency of the silver ion with ATH and the counter anion into the 1,2-dichloroethane. It is thought that before the phase transfer of the copolymer occurs, the silver ion was coordinated with sulfur atoms of ATH units in the copolymer. In this case, ATH-NIPAAm copolymer (1:84) in which the number of the ATH units was almost same as that of the silver ion in the solution. It was suggested that the ATH unit reacted with silver ion quantitatively [19]. Relatively higher energy might be required for the phase transfer when the polymer contained cations coordinated with ATH units because of their charges. However, the hydrophobic counter anion such as picrate ion is paired with the Ag-ATH for the charge compensation, it may cause the decrease of the LCST. Fig. 6 shows the effect of the metal ions on the phase transfer. In this case, excess amount of picrate ion over the metal ion was added to the copolymer solution. The curves for Ag(I) and Cu(I) and Au(III) are close to each other. It is thought that monovalent cations, silver and copper(I) form stable complex cation with ATH unit, and extracted into polymer phase with picrate ion. The curve for Au(III) was close to that for monovalent cations. Aurate ion may form chloro-complex such as [AuCl₂]⁺, which acts like monovalent cation, because the standard solution of Au(III) was generated with aqua regia. It is interesting that only the curve for Pd(II) ion shifted to the higher temperature. The LCST was 41.5 °C, much higher than that of PNIPAAm. The copolymer of ATH-NIPAAm in which the ATH unit coordinates to Pd(II) ion, might need higher energy for phase transfer accompanied dehydration.

3.3. Extraction behavior of metal ions

3.3.1. Metal ion selectivity

Metal ions such as Mg(II), Ca(II), Co(II), Zn(II), Ni(II), Mn(II), Fe(II), Cu(II), Cd(II), Cu(I), Pd(II), Ag(I) and Au(III) were examined for both of the liquid-liquid extraction and the copolymer extraction. Table 3 shows the extraction efficiency for each metal ion at pH 2–4. As described before [14], thiocrownether and acyclic polythioether are selective for soft metal ions, the so-called class *b* metal ions classified by Ahrlund. In both extraction systems, Mg(II) and

Table 3
Extraction efficiency of metal ion.

	Mg(II) <i>a</i>	Ca(II) <i>a</i>	Co(II) <i>ab</i>	Zn(II) <i>ab</i>	Ni(II) <i>ab</i>	Mn(II) <i>ab</i>	Fe(II) <i>ab</i>	Cu(II) <i>ab</i>	Cd(II) <i>b</i>	Cu(I) <i>b</i>	Pd(II) <i>b</i>	Ag(I) <i>b</i>	Au(III) <i>b</i>
Copolymer	0	0	0	0	0	0	0	0	0	97.04	94.8	96.16	97.92
Solvent extraction	0	0	0	0	0	0	0	0	0	98.96	83.56	97.28	95.19

Concentration of ATH, 2.5×10^{-5} M or ATH–NIPAAm (1:66), 0.025%, w/v; metal ion, 2.5×10^{-5} M; Na_2SO_4 , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; picrate ion, 1.0×10^{-3} M; NH_2OH , 3.3×10^{-2} M for Cu(I) and Fe(II); pH, 2–4.

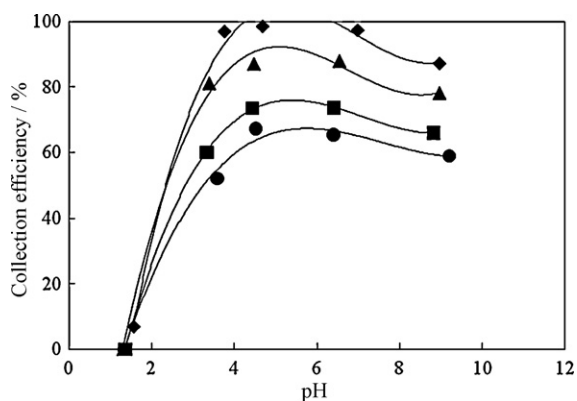


Fig. 7. Plots of extraction efficiency vs. pH. Concentration of ATH–NIPAAm (1:66), 0.025%, w/v; Cu(I) ion, 2.5×10^{-5} M; NH_2OH , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; counter anion, 1.0×10^{-3} M; counter anions: \blacklozenge , picrate ion; \blacktriangle , perchlorate ion; \blacksquare , nitrate ion; \bullet , none.

Ca(II) belonging to class *a* metal ions, and Co(II), Zn(II), Ni(II), Mn(II), Fe(II) and Cu(II) belonging to class *ab* metal ions were not extracted at all. On the other hand, class *b* metal ions with the exception of Cd(II) such as Cu(I), Pd(II), Ag(I) and Au(III) were extracted well. It is thought that the extraction efficiency reflects the stability of the metal–ATH complex formation. Both extraction systems were selective for class *b* metal ions. Therefore proposed extraction system using the ATH–NIPAAm copolymer in this study, performed as selective extraction system. However, at a pH higher than 7, metal hydroxide was adsorbed in the copolymer gel above the LCST. In this case masking agent such as tartarate may prevent the formation of metal hydroxide precipitation.

3.3.2. Effect of counter anion on copper(I) ion extraction

As shown in Fig. 7, the use of anions such as picrate, nitrate or perchlorate ion was effective for the extraction of copper(I) ion from the aqueous phase into the polymer phase. Especially, in the presence of picrate ion in the solution, more than 98% of copper(I) ion was extracted. Therefore, picrate ion was used for the other metal extractions.

3.3.3. Silver(I) ion extraction

Fig. 8 shows the extraction behavior of silver ion with the use of several copolymers containing ATH unit/NIPAAm unit (0:1–1:66). The extraction of silver(I) with PNIPAAm without ATH indicates that silver(I) ion was not extracted at all at the range of pH 2–6. It indicates that the N-isopropylacrylamide group does not work as extractant for silver ion. However, silver(I) ion was slightly extracted into PNIPAAm phase from the alkaline solution. It is thought that neutral silver oxide is precipitated in that pH region may be included into the solid polymer phase. On the other hand, the polymer containing both ATH group and NIPAAm group, extracts silver(I) well. The extraction efficiency of silver(I) ion increases similar to the increase of the ratio of ATH to NIPAAm. The copolymer with the ratio 1:66 might be sufficient for the extraction over 99% of silver(I) ion in the solution. The results indicate

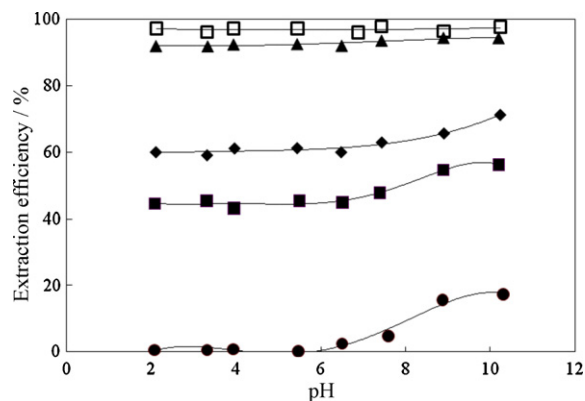


Fig. 8. Plots of extraction efficiency vs. pH. Concentration of ATH–NIPAAm, 0.025% (w/v); Ag(I) ion, 2.5×10^{-5} M; picrate ion, 1.0×10^{-3} M; Na_2SO_4 , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M. The ratio of ATH to NIPAAm: \square , 1:66; \triangle , 1:84; \diamond , 1:139; \blacksquare , 1:187; \bullet , PNIPAAm.

that ATH which has sulfur atoms like thioether group reacts with silver(I) ion and extracts it into polymer phase.

3.3.4. Copper(I) ion extraction

Fig. 9 shows the extraction behavior of copper(I) ion with the copolymer of ATH–NIPAAm. The results indicated that the increase of proton concentration causes the decrease of the extraction efficiency. This phenomenon might be because the decrease of reducing power of hydroxylamine permits the copper(II) ion as predominant species in such acidic solution. The extraction behavior was similar to liquid–liquid extraction behavior of Cu(I) using 1,2-dichloroethane as organic solvent. However, copper(I) was extracted well at the pH area of 3–6, when the copolymer in which the ratio of ATH to NIPAAm more than 1:84. It is thought that univalent metal ions such as silver(I) or copper(I) ion may form the 1:1 complex with ATH unit in the polymer chain. The order of the

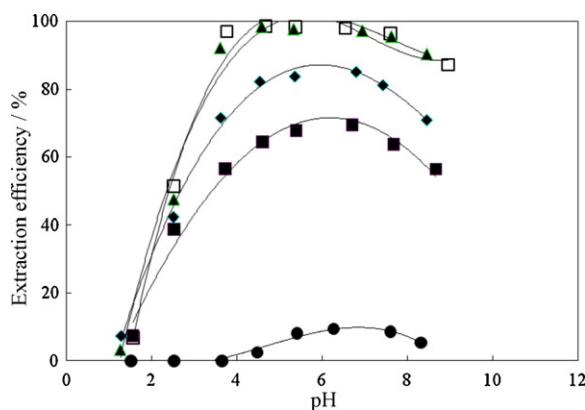


Fig. 9. Plots of extraction efficiency vs. pH. Concentration of ATH–NIPAAm, 0.025%, w/v; Cu(I) ion, 2.5×10^{-5} M; picrate ion, 1.0×10^{-3} M; Na_2SO_4 , NH_2OH , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M. The ratio of ATH to NIPAAm: \square , 1:66; \triangle , 1:84; \diamond , 1:139; \blacksquare , 1:187; \bullet , PNIPAAm.

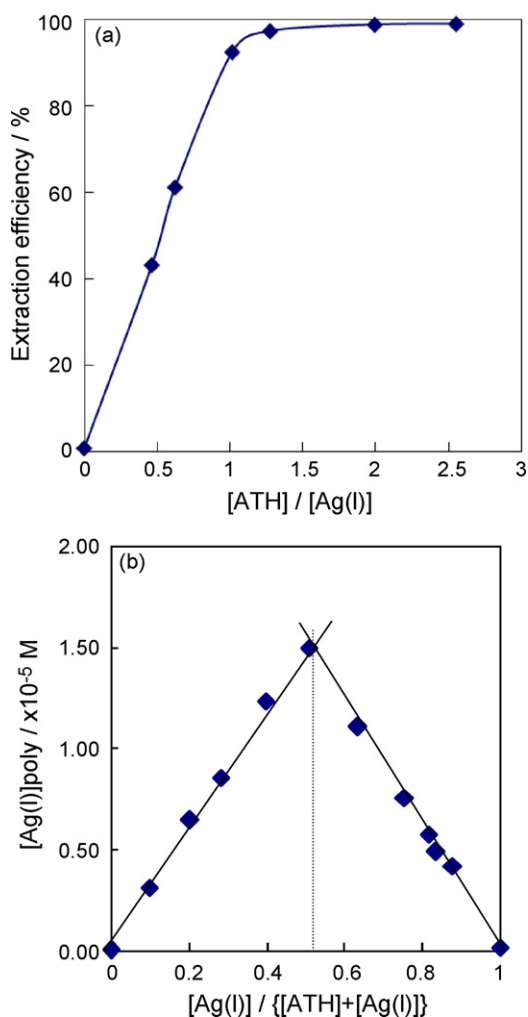


Fig. 10. (a) Plots of collection efficiency vs. $[ATH]/[Ag(I)]$. Concentration of $Ag(I)$ ion, 2.5×10^{-3} M; picrate ion, 1.0×10^{-3} M; Na_2SO_4 , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; pH, 4. (b) Plots of $[Ag(I)]_{poly} / \times 10^{-5}$ M vs. $[Ag(I)] / \{[ATH] + [Ag(I)]\}$. Concentration of picrate ion, 1.0×10^{-3} M; Na_2SO_4 , 3.3×10^{-2} M; buffer, 1.0×10^{-2} M; pH, 4.

extraction efficiency of copper(I) ion by each copolymer was consistent with that of the ratio of ATH to NIPAAm as well as silver ion.

3.3.5. Composition of the silver–ATH complex

As the concentration of ATH unit was determined by ICP–AES, it is possible to generate the concentrations of ATH in the solution. Quantitative extraction of metal ion indicates the molar ratio of metal ion complexes. Fig. 10(a) and (b) shows the result of the molar ratio method and the Job's plot. These indicate that Ag^+ forms 1:1 complex with ATH unit. The results for copper(I) extraction were the same as those for silver ion.

4. Conclusion

The physical property of the copolymer ATH–NIPAAm especially LCST changed with an increase in the ATH composition. Furthermore, when the ATH unit coordinated with Pd(II), the LCST shifted to higher temperature. The charge of Pd(II) ion might affect the phase transfer more than that of monovalent cations. It is an important investigation to control the LCST. Because, some thermoresponsive polymers are thought to be used for drug delivery systems in the human body. The present study demonstrates a possibility of separation of noble metal ions such as silver, copper and gold ions from the transition metals such as nickel, cobalt, iron, manganese and cadmium ions without using any organic solvent which are easily vaporized and highly toxic. The results also suggested that silver ion was not extracted at all by PNIPAAm without thioether unit. On the other hand, as the molar ratio of ATH unit increased, extraction efficiency of silver ion also increased. The results obtained were comparable with that of liquid–liquid extraction using the solvent 1,2-dichloroethane [19]. As the selectivity of ATH for noble metal ions such as silver(I), copper(I), gold(III) and palladium(II) ions was superior to that of classical reagent containing O-donor or N-donor atoms, it would be very useful to perform the extraction of noble metal ions with this kind of thermosensitive polymer including thioether units. Hybrid-type copolymers which have both thermoresponsive character and selective extraction, will be applicable in not only the simple extraction of metal ions but also other separation methods including electrophoresis and chromatography.

Acknowledgements

This work was supported by JSPS20550089, Grant-in-Aid for Scientific Research(C). Authors express their gratitude for Kojin Co., Japan for providing PIPAAm and NIPAAm monomer.

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