Formation of Thermosensitive Water-Soluble Copolymers with Phosphinic Acid Groups and the Thermosensitivity of the Copolymers and Copolymer/Metal Complexes

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ABSTRACT: Thermosensitive and water-soluble copolymers were prepared through the copolymerization of acryloyloxypropyl phosphinic acid (APPA) and *N*-isopropyl acrylamide (NIPAAm). The thermosensitivity of the copolymers and copolymer/metal complexes was studied. The APPA–NIPAAm copolymers with less than 11 mol % APPA moiety had a lower critical solution temperature (LCST) of approximately 45°C, but the APPA–NIPAAm copolymers with greater than 21 mol % APPA moiety had no LCST from 25 to 55°C. The APPA–NIPAAm copolymers had a higher adsorption capacity for Sm^{3+}, Nd^{3+}, and La^{3+} than for Cu^{2+}, Ni^{2+} and Co^{2+}. The APPA–NIPAAm (10:90) copolymer/metal (Sm^{3+}, Nd^{3+}, or La^{3+}) complexes became water-insoluble above 45°C at pH 6–7, but the APPA–NIPAAm (10:90) copolymer/metal (Cu^{2+},Ni^{2+}, or Co^{2+}) complexes were water-soluble from 25 to 55°C at pH 6–7. The temperature at which both the APPA–NIPAAm copolymers and the copolymer/metal complexes became water-insoluble increased as the pH values of the solutions increased. The APPA–NIPAAm copolymers were able to separate metal ions from their mixed solutions when the temperature of the solutions was changed; this was followed by centrifugation of the copolymer/metal complexes after the copolymers were added to the metal solutions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 116–125, 2004

Key words: adsorption; stimuli-sensitive polymers; water-soluble polymers

INTRODUCTION

Poly(*N*-isopropyl acrylamide) (polyNIPAAm) is a thermosensitive polymer with a lower critical solution temperature (LCST) in an aqueous solution of approximately 32°C. Copolymers containing polyNIPAAm have been widely studied from fundamental and practical points of views.[1–15] We have reported that thermosensitive copolymer hydrogels with phosphonium groups have a high absorption capacity for water and a high antibacterial activity against bacteria such as *Staphylococcus aureus* and *Escherichia coli* and that their water absorption capacity and antibacterial activity depend on the temperature of the solutions.[16,17] So far, only a few reports on the synthesis of thermosensitive water-soluble copolymers with an adsorption capacity for metal ions have been published.[18,19] This report concerns with the preparation of thermosensitive water-soluble polymers with phosphinic acid groups through the copolymerization of acryloyloxypropyl phosphinic acid (APPA) and *N*-isopropyl acrylamide (NIPAAm) and the adsorption capacity of the obtained APPA–NIPAAm copolymers for metal ions such as Sm^{3+}, La^{3+}, Nd^{3+}, Cu^{2+}, Co^{2+}, and Ni^{2+}. The thermosensitivity of the solutions of the APPA–NIPAAm copolymers and the copolymer/metal complexes was also investigated in the absence and presence of NaCl and at various pHs. The possibility of the copolymers being used for the separation of metal ions in aqueous solutions was also investigated.

EXPERIMENTAL

Materials

APPA and NIPAAm were kindly supplied by Nippon Kagaku Kogyo Co. and Kohjin Co. (Tokyo, Japan), respectively, and were used without further purification. 2,2′-Azobisisobutylonitrile (AIBN; Nacalai Tesque Co. Kyoto, Japan) was purified by recrystallization from ethanol (Wako Pure Chemical Industries, Ltd. Osaka, Japan). Other chemical compounds were reagent-grade and were used as received.

Synthesis of the water-soluble APPA–NIPAAm copolymers

The structure of the APPA–NIPAAm copolymers is shown in Figure 1. First, APPA and NIPAAm (2 g total) were dissolved in 10 cm^3 of dimethyl sulfoxide (DMSO) in a glass vessel under a nitrogen atmo-

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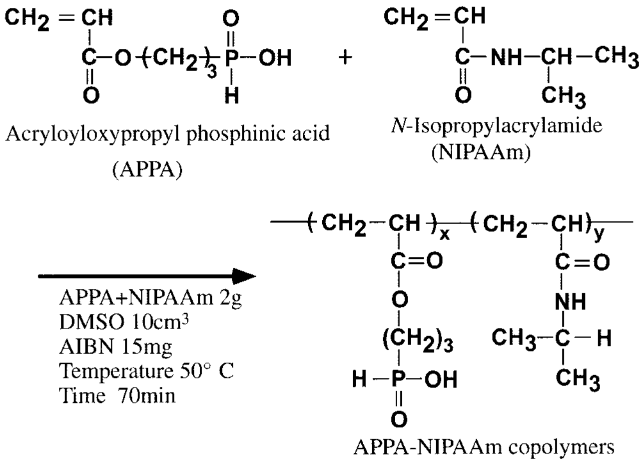

Figure 1 Synthesis of APPA–NIPAAm copolymers.

sphere. The molar ratio of APPA to NIPAAm in the feed was varied from 7:93 to 40:60. The copolymers were obtained by radical copolymerization with AIBN (15 mg) as a radical initiator at 50°C for 70 min in sealed ampules under a nitrogen atmosphere. After polymerization, the polymer mixture was dissolved in deionized water. The copolymers were purified by dialysis against the deionized water, and then the copolymers were obtained by freeze drying. The content of the phosphinic acid groups in the copolymers was calculated from the phosphorus content of the dried copolymers. The phosphorus content was determined as follows. Dried copolymers (0.1 g) and 70% nitric acid (10 cm^3) were placed in a Kjeldahl flask; the mixture was heated until white steam came out, and then it was cooled. After that, 60% perchloric acid (10 cm^3) was added to the solution, and the mixture was heated until the solution became transparent. The concentration of phosphoric acid in the resultant solution was determined by the phosphovanadomolybdate method.[20] The nitrogen content, which corresponded to the NIPAAm content in the copolymers, was determined by elemental analysis (CHN Corder MT-6, Yanaco, Kyoto, Japan).

Measurement of the molecular weight of the APPA–NIPAAm copolymers

The molecular weight and molecular weight distribution were determined with gel permeation chromatography (GPC) with a refractive-index detector (RID-10A, Shimadzu, Kyoto, Japan) with a Shim-Pack 806 column. The samples were measured against poly(ethylene oxide) standards with a 0.05 mol/dm^3 LiBr/dimethylformamide (DMF) solution as the mobile phase. The flow rate was 1.0 cm^3/min.

Measurement of the thermosensitivity of the APPA–NIPAAm copolymers

The thermosensitivity of the APPA–NIPAAm copolymers and copolymer/metal complexes was evaluated with the transmittance of their solutions at 660 nm at various temperatures in the absence or presence of NaCl and at various pHs.

Measurement of the adsorption capacity of the copolymers for metal ions

A 5-cm^3 copolymer solution (5 g/dm^3) was placed in a cellophane tube and was soaked in 30-cm^3 metal-ion solutions at 30°C for 24 h. The adsorption capacity was calculated through the determination of the concentration of residual metal ions in the outer solutions with inductively coupled argon plasma atomic emission spectrophotometry (ICPS-5000, Shimadzu).

Removal of metal ions with the copolymers from their solutions

The APPA–NIPAAm copolymer solutions were added to metal-ion solutions, and the solutions were shaken at 30°C for 30 min and then allowed to stand at 60°C for 1 h. After that, the copolymer/metal complexes were centrifuged at 10,000 ppm for 1 min. The removal (%) of the metal ions was calculated through the determination of the residual metal-ion concentrations of the supernatants with inductively coupled argon plasma atomic emission spectrophotometry (ICPS-5000, Shimadzu).

RESULTS AND DISCUSSION

Synthesis of the APPA–NIPAAm copolymers

Table I shows the properties of the APPA–NIPAAm copolymers. The copolymers, having different compositions, were obtained through variations in the molar ratio of APPA to NIPAAm in the feed from 7:93 to 40:60. The composition of the copolymers was calculated with the ratio of P (%) to N (%) from the elemental analysis of the copolymers. Table I shows that APPA–NIPAAm copolymers with various compositions could be arbitrarily obtained through variations in the APPA content in the feed. The copolymers had molecular weights of 25,500–36,300, and the magnitude of the molecular weight of the copolymers was independent of the composition of the copolymers. The molecular weight of the APPA–NIPAAm (40:60) copolymer with the highest content of APPA moieties could not be determined by this method because a 2.5% (w/v) APPA–NIPAAm (40:60) copolymer solution did not become a complete solution and instead became a highly viscous DMF solution. Table I also shows the content of phosphinic acid groups in the

TABLE I
Properties of the APPA–NIPAAm Copolymers

Copolymer abbreviation	Molar ratio in the feed (APPA:NIPAAm)	Molar ratio in the copolymer (APPA:NIPAAm)[a]	M_n (g/mol)[b]	M_w/M_n[b]	Phosphinic acid group (mmol/g)
APPA–NIPAAm (7:93)	7:93	9.5:90.5	36,300	1.74	0.75
APPA–NIPAAm (10:90)	10:90	11.3:88.7	25,500	1.50	0.8
APPA–NIPAAm (20:80)	20:80	20.8:79.2	30,400	1.97	1.2
APPA–NIPAAm (30:70)	30:70	28.7:71.3	29,700	1.47	1.6
APPA–NIPAAm (40:60)	40:60	38.9:61.1	—	—	2.0

[a] The composition of the copolymers was calculated from P (%)/N (%) by elemental analysis.

[b] M_n = number-average molecular weight; M_w = weight-average molecular weight. These values were determined by GPC with poly(ethylene oxide) standards in a DMF solution of 0.05 mol/dm^3 of LiBr.

[c] The content of phosphinic acid groups was calculated from the P content in the copolymers.

copolymers calculated from the P contents of the copolymers. The structure of the copolymers was also confirmed by Fourier transform infrared spectroscopy (Spectrum One, PerkinElmer, Boston, MA).

Thermosensitivity of the APPA–NIPAAm copolymers in water in the absence or presence of NaCl

The thermosensitivity of the APPA–NIPAAm (10:90–40:60) copolymers in water was evaluated from the transmittance at 660 nm of copolymer solutions (5 g/dm^3) at various temperatures in the absence or presence of NaCl (Fig. 2). PolyNIPAAm is known to have an LCST of approximately 32°C. This means that polyNIPAAm dissolves in water below 32°C but does not dissolve above that temperature. The transmittance of polyNIPAAm solutions is also shown in Figure 2. The transmittance of the solutions of the APPA–NIPAAm (10:90) copolymer in the absence of NaCl decreased abruptly above 40°C, but the transmittance of a solution of the APPA–NIPAAm (20:80) copolymer began to decrease gradually above 50°C. The LCST of the APPA–NIPAAm (20:80) copolymer is not clear. Furthermore, the transmittance of the APPA–NIPAAm (30:70) copolymer solutions hardly decreased from 25 to 60°C. The APPA–NIPAAm (40:60) copolymer exhibited almost the same behavior as the APPA–NIPAAm (30:70) copolymer. These results indicate that the introduction of much APPA into polyNIPAAm made the copolymers more hydrophilic and water-soluble even above 45°C.

In the presence of NaCl, the transmittance of the APPA–NIPAAm (10:90) copolymer solutions increased as the NaCl concentration increased up to 0.05 mol/dm^3, with the one exception of a 0.01 mol/dm^3 NaCl solution. A similar phenomenon was also observed with the APPA–NIPAAm (7:93) copolymer, which had a lower APPA content than the APPA–NIPAAm (10:90) copolymer. An analogous phenomenon was reported for polypeptides in aqueous NaCl solutions.[21] This means that the addition of NaCl to water made the polymers more hydrophilic. However, the exact reason for the increase in the transmittance of these polymer solutions as the NaCl concen-

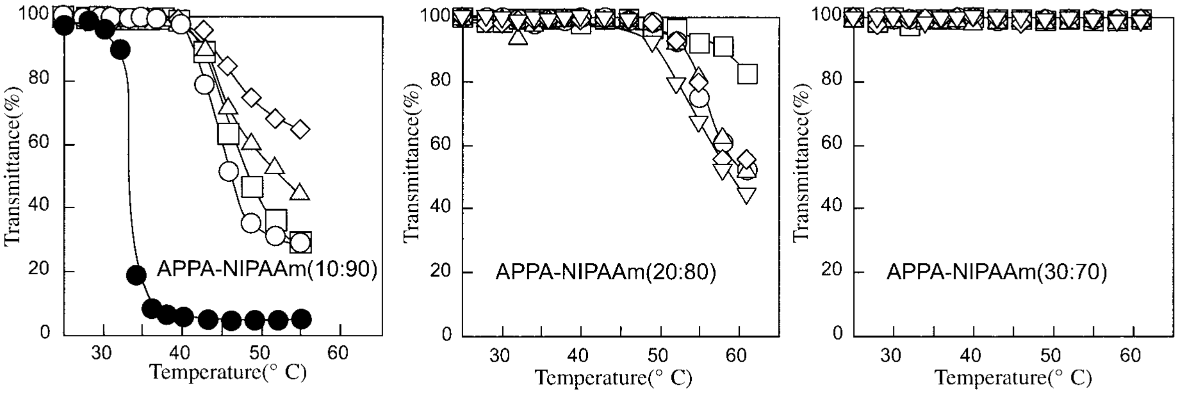

Figure 2 Temperature dependence of the transmittance at 660 nm of APPA–NIPAAm (10:90, 20:80, and 30:70) copolymer solutions in the absence or presence of NaCl (concentration of the copolymer solution = 5 g/dm^3). The concentrations of NaCl were (□) 0, (○) 0.01, (△) 0.03, (◇) 0.05, and (▽) 0.10. The solid circles represent polyNIPAAm (number-average molecular weight = 354,000 and weight-average molecular weight/number-average molecular weight = 3.0).

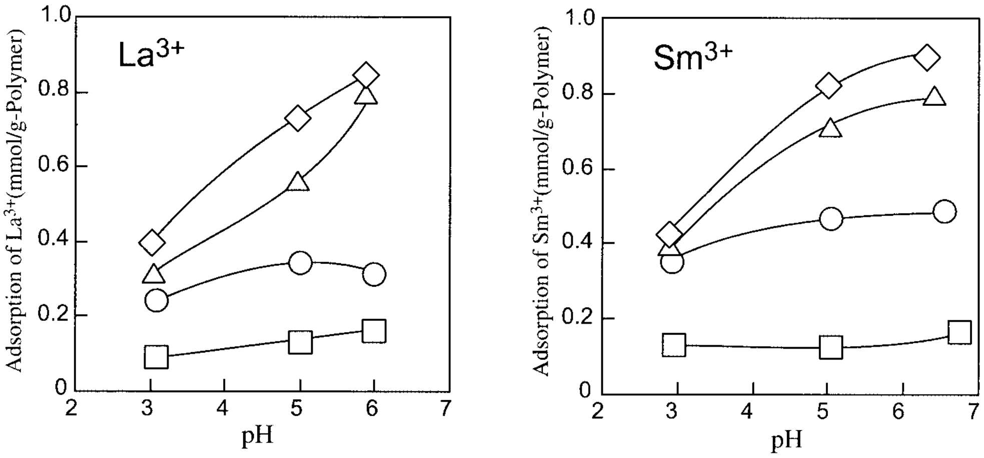

Figure 3 Effect of pH on the adsorption of metal ions with APPA–NIPAAm copolymers in the pH range of 3–7 [polymer solution (2.5 g/dm^3) = 4 cm^3; metal-ion solution (1.5 × 10^{-3} mol/dm^3) = 30 cm^3; buffer solution = $CH_3COOH—CH_3COONa$; period of shaking at 30°C = 24 h]. The APPA–NIPAAm copolymers were (□) 10:90, (○) 20:80, (△) 30:70, and (◇) 40:60.

tration increased has not been clarified yet. The degree of the decrease in the transmittance of the APPA–NIPAAm (20:80) copolymer solution with increasing temperature increased with the addition of NaCl. This was due to both the shielding effect of the charges on the copolymers and the dehydration effect by NaCl addition. However, the transmittances of the APPA–NIPAAm (30:70) copolymer solutions hardly decreased from 25 to 60°C and were almost 100%, even in an aqueous solution of 0.1 mol/dm^3 NaCl. A similar phenomenon was also observed with the APPA–NIPAAm (40:60) copolymer. This can be explained by the introduction of much APPA (phosphinic acid groups) into the APPA–NIPAAm copolymer.

Adsorption capacity of the APPA–NIPAAm copolymers for metal ions

The adsorption capacity of the APPA–NIPAAm (10:90–40:60) copolymers for La^{3+}, Nd^{3+}, and Sm^{3+} was measured at various pHs. The results for the adsorption of La^{3+} and Sm^{3+} are shown in Figure 3. The adsorption capacity for La^{3+} and Sm^{3+} increased with an increasing content of the APPA moiety in the copolymers and an increasing pH of the solutions. A similar adsorption tendency was obtained for Nd^{3+}. The adsorption capacity of the copolymers for Cu^{2+}, Co^{2+}, and Ni^{2+} was also measured at various pHs. The results for the adsorption of Cu^{2+} and Ni^{2+}are shown in Figure 4. Figure 4 also shows that the adsorption capacity for Cu^{2+} and Ni^{2+} increased with an increasing content of the APPA moiety in the copolymers and with an increasing pH of the solutions. A similar adsorption tendency was obtained for Co^{2+}. These results indicate that these metal ions were adsorbed by coordinate bonds with phosphinic acid groups in the copolymers. Figures 3 and 4 show that the adsorption capacities for Cu^{2+}, Co^{2+}, and Ni^{2+} were smaller than those for La^{3+}, Nd^{3+}, and Sm^{3+}.

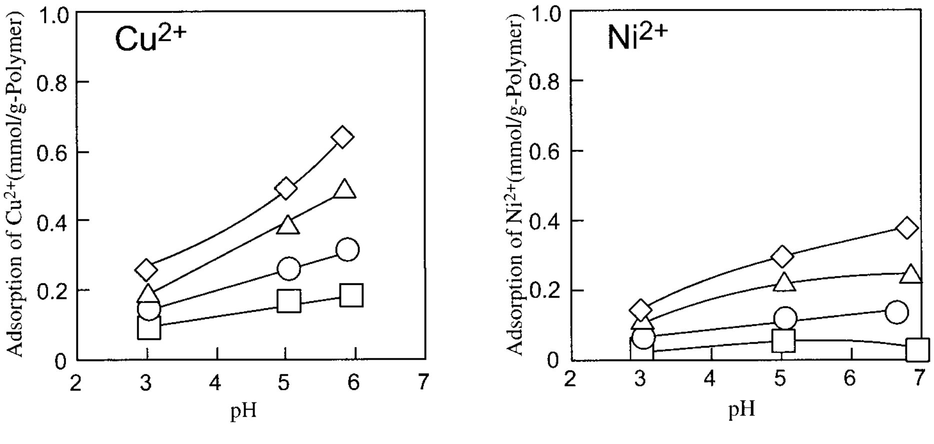

Figure 4 Effect of pH on the adsorption of metal ions with APPA–NIPAAm copolymers in the pH range of 3–7 [polymer solution (2.5 g/dm^3) = 4 cm^3; metal-ion solution (1.5 × 10^{-3} mol/dm^3) = 30 cm^3; buffer solution = $CH_3COOH—CH_3COONa$; period of shaking at 30°C = 24 h]. The APPA–NIPAAm copolymers were (□) 10:90, (○) 20:80, (△) 30:70, and (◇) 40:60.

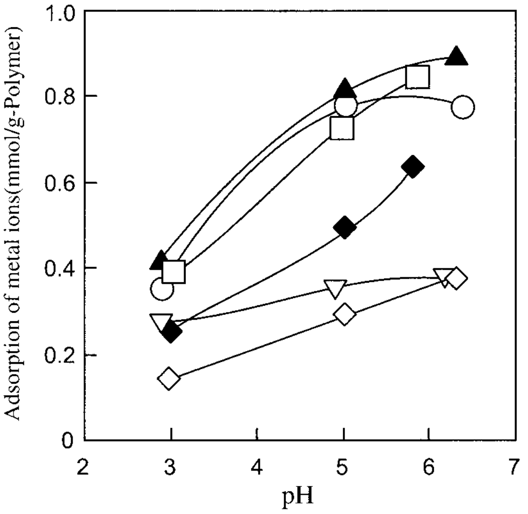

Figure 5 Effect of pH on the adsorption of metal ions with an APPA–NIPAAm (40:60) copolymer [polymer solution (2.5 g/dm^3) = 4 cm^3; metal-ion solution (1.5 × 10^{-3} mol/dm^3) = 30 cm^3; buffer solution = CH_3COOH—CH_3COONa; period of shaking at 30°C = 24 h]. The metal ions were (▲) Sm^{3+}, (○) Nd^{3+}, (□) La^{3+}, (◆) Cu^{2+}, (▽) Co^{2+}, and (◇) Ni^{2+}.

Figure 5 shows the adsorption capacity of the APPA–NIPAAm (40:60) copolymer for various metal ions at various pHs.

The order of the adsorption capacity for the metal ions was as follows: Sm^{3+}, Nd^{3+}, La^{3+} > Cu^{2+} > Co^{2+} > Ni^{2+}. That is, the APPA–NIPAAm copolymers had a higher adsorption capacity for lanthanoid metal ions than for transition-metal ions.

Effect of temperature on the adsorption of metal ions

We mentioned before that the APPA–NIPAAm (10:90) and APPA–NIPAAm (20:80) copolymer began to be water-insoluble above 40 and 50°C in water, respectively, and that the APPA–NIPAAm (30:70) and APPA–NIPAAm (40:60) copolymers were water-soluble even above 55°C. The adsorption capacity of the APPA–NIPAAm (10:90–40:60) copolymers for metal ions (La^{3+}, Nd^{3+}, Sm^{3+}, and Cu^{2+}) was measured at various temperatures. The results for Nd^{3+} and Cu^{2+} are shown in Figure 6. In both cases, the adsorption capacity for the metal ions increased as the temperature increased up to 30°C and then decreased with increasing temperature. The decrease in the adsorption capacity for metal ions with increasing temperature was due to the change in the hydrophilic–hydrophobic balance of the copolymers in water above the LCST (ca. 32°C) of the polyNIPAAm chains in the copolymers, although an obvious decrease in the transmittance of the copolymer solutions was not observed near the LCST of polyNIPAAm.

Thermosensitivity of the APPA–NIPAAm copolymer/metal complexes

The thermosensitivity of the APPA–NIPAAm copolymer/metal complexes in water was evaluated from the transmittance at 660 nm of the copolymer/metal complex solutions at various temperatures. The APPA–NIPAAm (10:90) and APPA–NIPAAm (40:60) copolymers were used for this experiment. The results are shown in Figure 7. The transmittance of the APPA–NIPAAm (10:90) copolymer/Sm^{3+} complex solution decreased abruptly above 43°C. The transmittance of the copolymer/Sm^{3+} complex solution became almost zero at 49°C, and then it increased slightly with increasing temperature. This slight increase in the transmittance was due to the formation of a precipitate of the copolymer/Sm^{3+} complex above 50°C. The temperature at which the transmit-

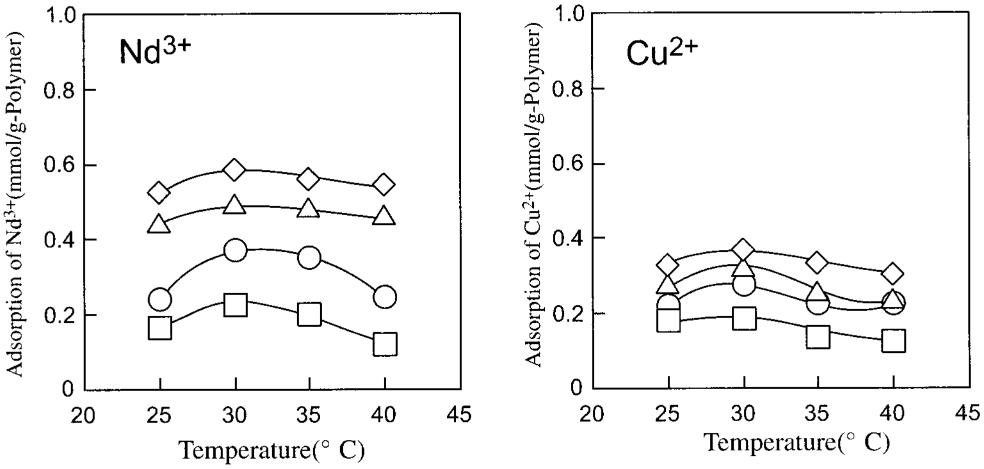

Figure 6 Temperature dependence of the adsorption of metal ions with APPA–NIPAAm copolymers [polymer solution (2.5 g/dm^3) = 4 cm^3; metal-ion solution (1.5 × 10^{-3} mol/dm^3) = 30 cm^3; period of shaking at 30°C = 24 h]. The APPA–NIPAAm copolymers were (□) 10:90, (○) 20:80, (△) 30:70, and (◇) 40:60.

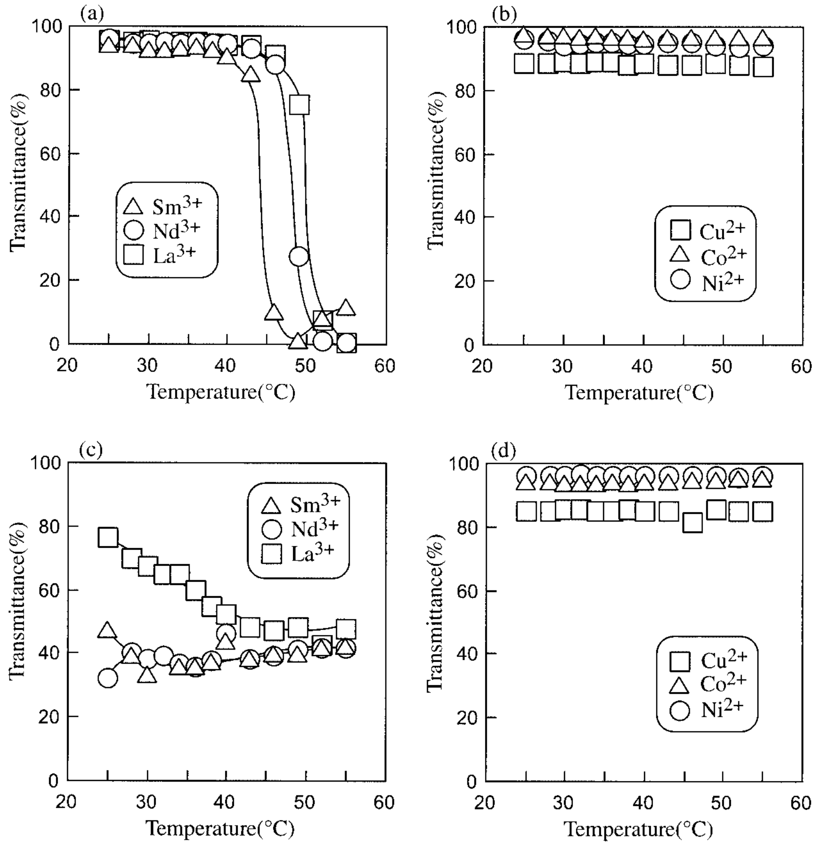

Figure 7 Temperature dependence of the transmittance at 660 nm of APPA–NIPAAm copolymer/metal complex solutions at pH 6–7 (concentration of the copolymer = 2.5 g/dm^3). The APPA–NIPAAm copolymers were (a,b) 10:90 and (c,d) 40:60.

tance of the APPA–NIPAAm (10:90)/Nd^{3+} and APPA–NIPAAm (10:90)/La^{3+} complex solutions began to decrease abruptly shifted slightly to a temperature higher than 48°C. The transmittance of the copolymer/Nd^{3+} and copolymer/La^{3+} complex solutions became almost zero above 52 and 55°C, respectively. The abrupt decrease in the transmittance of the APPA–NIPAAm (10:90)/metal (Sm^{3+}, Nd^{3+}, and La^{3+}) complex solutions with increasing temperature indicated that the insolubilization of the copolymers in water was accelerated by the formation of the APPA–NIPAAm (10:90) copolymer/metal (Sm^{3+}, Nd^{3+}, and La^{3+}) complexes.

However, the transmittance of the APPA–NIPAAm (10:90) copolymer/metal (Cu^{2+}, Ni^{2+}, and Co^{2+}) complex solutions hardly decreased in the temperature range studied. This phenomenon indicates that the APPA–NIPAAm (10:90) copolymer became more hydrophilic through the adsorption of metal ions such as Cu^{2+}, Ni^{2+}, or Co^{2+}.

We mentioned before that the transmittance of the APPA–NIPAAm (40:60) copolymer solution hardly changed from 25 to 60°C and that it was almost 100%. Figure 7(c) shows that the transmittance of the APPA–NIPAAm (40:60) copolymer/La^{3+} complex solution decreased gradually from 80 to 45% with increasing temperature. The transmittances of the copolymer/Sm^{3+} and copolymer/Nd^{3+} complex solutions were not dependent on the temperature; they were about 40%. The transmittances of the APPA–NIPAAm (40:60) copolymer/metal (Cu^{2+}, Ni^{2+}, or Co^{2+}) complex solutions hardly decreased in the temperature range studied, and the same was true for the APPA–NIPAAm (10:90) copolymer/metal (Cu^{2+}, Ni^{2+}, or Co^{2+}) complexes. These results suggest that Sm^{3+}, Nd^{3+}, and La^{3+} made the copolymers more hydrophobic but Cu^{2+}, Ni^{2+}, and Co^{2+} made the copolymers more hydrophilic by their adsorption onto the copolymers.

Effect of the molar ratio of added metal ions to the copolymers on the thermosensitivity of the copolymers

The transmittances of the solutions of the APPA–NIPAAm (10:90) copolymer/La^{3+} and APPA–NIPAAm (10:90) copolymer/Cu^{2+} complexes, which were obtained through changes in the molar ratio of metal ions to phosphinic acid groups in the copolymers, were measured at various temperatures (Fig. 8). The temperature dependence of the transmittance of the copolymer/La^{3+} complex solution increased with

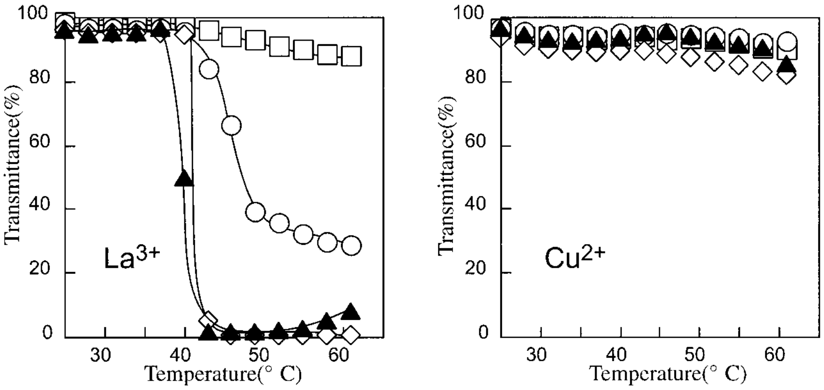

Figure 8 Temperature dependence of the transmittance at 660 nm of APPA–NIPAAm (10:90) copolymer/metal complex solutions (concentration of the copolymer = 2.5 g/dm^3). The molar ratios of added metal ions to phosphinic acid groups in the copolymer were (□) 0.5, (○) 1.0, (◇) 2.0, and (▲) 4.0.

an increasing molar ratio of added metal ions to phosphinic acid groups in the copolymers. In particular, the transmittance of solutions of the APPA–NIPAAm copolymer/La^{3+} complex decreased abruptly above around 40°C when the molar ratios of added metal ions to phosphinic acid groups in the copolymers were greater than 2. However, the transmittance of the copolymer/Cu^{2+} complex solution hardly decreased with increasing temperature, even when the molar ratio of metal ions to phosphinic acid groups in the copolymer was 4. These results suggest that the addition of La^{3+} made the APPA–NIPAAm (10:90) copolymer hydrophobic, but the addition of Cu^{2+} made the copolymer hydrophilic.

Adsorption ability of the APPA–NIPAAm copolymers for metal ions from metal solutions of various initial concentrations

To clarify the reason for the difference in the temperature dependence of the transmittance between the copolymer/metal (La^{3+}, Nd^{3+}, and Sm^{3+}) and copolymer/metal (Cu^{2+}, Co^{2+}, and Ni^{2+}) complex solutions, the adsorption of metal ions with the APPA–NIPAAm (10:90) copolymer from metal solutions of various initial concentrations was investigated. The results for La^{3+} and Cu^{2+} are shown in Figure 9. The ratio of added metal ions to phosphinic acid groups in the copolymers was varied from 0.5 to 4.0. In both cases, the adsorption of metal ions increased with an increasing initial metal-ion concentration in the solutions. In particular, the adsorption of metal ions increased sharply with an increasing molar ratio of added metal ions to phosphinic acid groups in the copolymer up to a molar ratio of 2 and then increased gradually. The adsorption of La^{3+} and Cu^{2+} at a molar ratio of 4 of added metal ions to phosphinic acid groups in the copolymers was 0.19 and 0.12 mmol/g, respectively. These values were less than one-third of the phosphinic acid group content (0.72 mmol/g) of the APPA–NIPAAm copolymers. As shown in Figure 8, the transmittance of the copolymer/La^{3+} complex solution decreased with an increasing molar ratio of added metal ions to phosphinic groups in the copolymers. In particular, it decreased abruptly when the molar ratio of La^{3+} to phosphinic acid groups was greater than 2. This result indicates that the copolymer/La^{3+} complex became more hydrophobic through the adsorption of La^{3+} with the copolymers. We mentioned that metal ions were adsorbed via coordinate bonds with phosphinic acid groups in the copolymers. Therefore, the copolymers could be crosslinked with metal ions when metal ions were

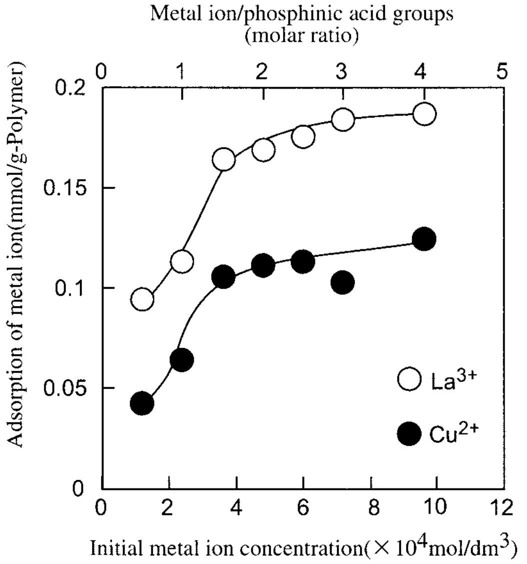

Figure 9 Adsorption of metal ions (La^{3+} and Cu^{2+}) from solutions of various initial metal concentrations [P content of the APPA–NIPAAm (10:90) copolymer = 0.72 mmol/g; polymer solution (2.5 g/dm^3) = 4 cm^3; metal-ion solution = 30 cm^3; period of shaking at 30°C = 24 h].

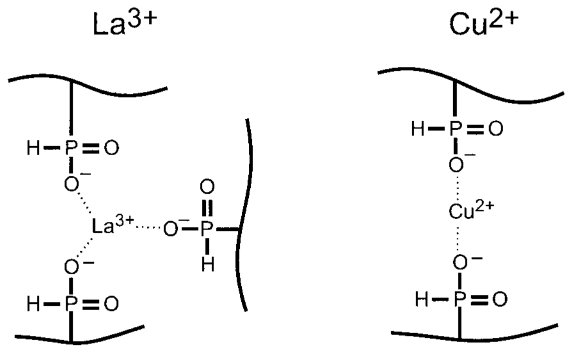

Figure 10 Crosslinking of APPA–NIPAAm copolymers with La^{3+} and Cu^{2+}.

adsorbed onto the copolymers, as shown in Figure 10. This crosslinking of the copolymers with La^{3+} must be stronger than that with Cu^{2+} because La^{3+} is a trivalent cation and Cu^{2+} is a divalent cation. The higher hydrophobicity of the APPA–NIPAAm/La^{3+} complex, with respect to that of the copolymer/Cu^{2+} complex, was due to the higher adsorption of La^{3+} and the resultant stronger crosslinking of the copolymers with La^{3+} than with Cu^{2+}. Moreover, some water molecules were bound to each metal ion adsorbed on the copolymers. However, the exact reason that the copolymer/Cu^{2+} complex became more hydrophilic is still unclear, and further investigation is needed.

Effect of pH on the temperature dependence of the transmittance of the copolymer/metal complex solutions

The transmittance of the APPA–NIPAAm copolymer/metal complex solutions at 660 nm was measured at various temperatures at pH 3.5 and pH 6.5. The APPA–NIPAAm (7:93) copolymer was used for this experiment. The temperature dependence of the transmittance of the APPA–NIPAAm (7:93) copolymer/metal (Sm^{3+} or Cu^{2+}) complex solution is shown in Figure 11. The transmittance of the APPA–NIPAAm (7:93)/Sm^{3+} complex solution at pH 3.5 began to decrease above 35°C, and it became almost zero at 38°C; then, it increased again as the temperature increased above 43°C. The increase in the transmittance with increasing temperature was due to the increasing formation of the precipitates of the copolymer/Sm^{3+} complexes above 43°C. However, at pH 6.5, the transmittance of the copolymer/Sm^{3+} complex solution decreased abruptly above 43°C, and it became almost zero above 48°C. This result indicates that the copolymer/Sm^{3+} complex became more hydrophilic at pH 6.5 than at pH 3.5. This was due to the greater dissociation of phosphinic acid groups at pH 6.5 than at pH 3.5 because the pK_a value of poly(acryloyloxypropyl phosphinic acid) was found to be about 4.1. A similar phenomenon was also observed for the copolymer/La^{3+} and copolymer/Nd^{3+} complexes, although the temperatures at which the transmittance of the copolymer/metal complex solutions decreased abruptly were a little bit different. However, the transmittance of the APPA–NIPAAm (7:93)copolymer/Cu^{2+} complex solution at pH 3.5 decreased gradually as the temperature increased above 38°C to about 60% at 55°C, but the transmittances of the copolymer/Cu^{2+} complex solution at pH 6.5 hardly decreased from 25 to 55°C, and they were about 90%. Similar phenomena were also observed for the copolymer/Co^{2+} or copolymer/Ni^{2+} complexes. Thus, the pH of the solutions greatly affected the hydrophilicity of the copolymer/metal complexes in water.

Adsorption of metal ions from mixed metal-ion solutions

The adsorption of metal ions with APPA–NIPAAm copolymers from mixed metal-ion solutions was measured by an equilibrium method at 30°C for 24 h. The mixed metal-ion solutions contained each metal ion at the same concentration of 1.5×10^{-3} mol/dm^3. The

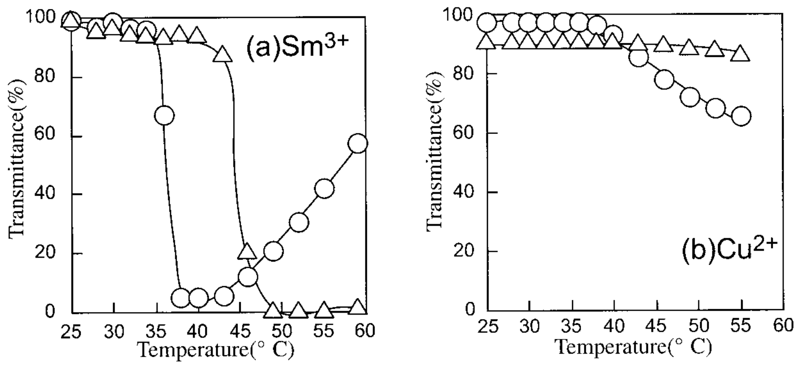

Figure 11 Temperature dependence of the transmittance at 660 nm of APPA–NIPAAm (7:93) copolymer/metal complex solutions at (○) pH 3.4 and (△) pH 6.5 (concentration of the polymer = 2.5 g/dm^3; added metal ions/phosphinic acid groups in the copolymer = 6/1 mol/mol).

molar ratio of added metal ions to phosphinic acid groups in the copolymer was 4:1. The results for the adsorption of each metal ion from La^{3+}, Nd^{3+}, and Sm^{3+}/Cu^{2+} mixed solutions are shown in Figure 12. Figure 12 shows that the copolymer had a higher selective adsorption capacity for La^{3+}, Nd^{3+}, and Sm^{3+} than for Cu^{2+} from their mixed solutions than expected from the adsorption capacity from their single-metal-ion solutions.

Removal of metal ions with the APPA–NIPAAm copolymers

We mentioned before that the APPA–NIPAAm copolymer/metal (La^{3+}, Nd^{3+}, Sm^{3+}) complexes precipitated above the temperature at which the transmittance of the respective copolymer/metal complex solution became almost zero. This indicates that the metal ions could be removed from their metal solutions through the formation of the copolymer/metal complexes, followed by centrifugation of the precipitates, after the solution temperature was raised above the temperature at which the copolymer/metal complexes were precipitated. The removal of metal ions from their mixed metal-ion solutions was investigated (Fig. 13). In this case, an equivalent mole of phosphinic acid groups was added to metal-ion solutions. In all cases, a higher selective removal (%) of lanthanoids (La^{3+}, Nd^{3+}, and Sm^{3+}), with respect to Cu^{2+}, than expected from the selective adsorption by the equilibrium dialysis method was obtained from their mixed solutions. The order of the selective removal of lanthanoids with respect to Cu^{2+} was $Sm^{3+} > Nd^{3+} > La^{3+}$. Thus, the APPA–NIPAAm copolymers were able to separate metal ions from their mixed solutions through changes in the temperature of the solutions after the copolymers were added to metal-ion solutions.

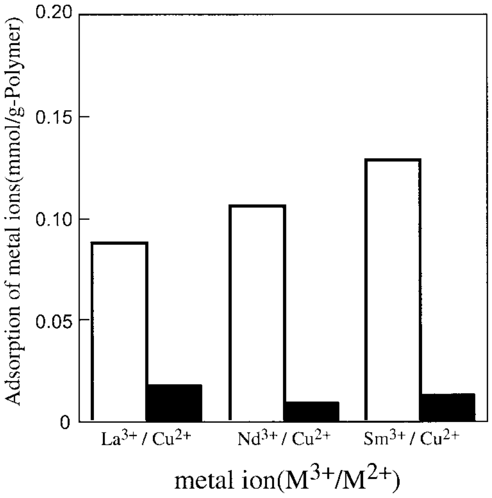

Figure 12 Adsorption of metal ions with APPA–NIPAAm copolymers from mixed metal-ion solutions by the equilibrium dialysis method [P content = 0.34 mmol/g; polymer solution (5 g/dm^3) = 5 cm^3; metal-ion solution (1.5×10^{-3} mol/dm^3) = 25 cm^3; period of shaking at 30°C = 24 h; added metal ions/phosphinic acid groups in the copolymer = 4/1 mol/mol].

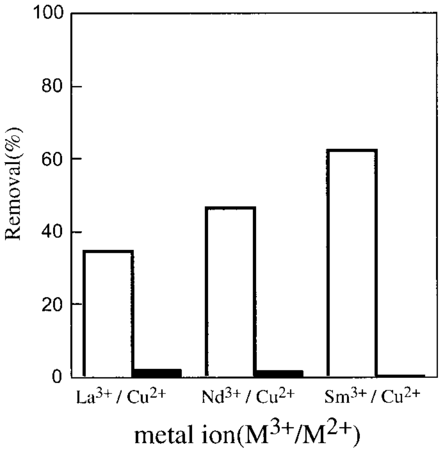

Figure 13 Removal of metal ions from mixed metal-ion solutions with the APPA–NIPAAm copolymer [P content = 0.34 mmol/g; polymer solution (10 g/dm^3) = 10 cm^3; metal-ion solution (1.7×10^{-3} mol/dm^3) = 10 cm^3; metal ions/phosphinic acid groups = 1/1 mol/mol]. The metal-ion concentrations of the supernatants were measured after centrifugation at 10,000 rpm for 1 min, after polymer/metal complexes were allowed to stand at 60°C for 1 h after mixed polymer solutions were shaken with metal-ion solutions at 30°C for 30 min.

CONCLUSIONS

1. Thermosensitive and water-soluble copolymers with an adsorption capacity for metal ions were prepared by the copolymerization of APPA and NIPAAm.
2. The APPA–NIPAAm copolymers with less than about 11 mol % APPA moiety had an LCST of approximately 45°C, but the APPA–NIPAAm copolymers with greater than 21 mol % APPA moiety had no LCST from 25 to 55°C.
3. The APPA–NIPAAm copolymers had a higher adsorption capacity for Sm^{3+}, Nd^{3+}, and La^{3+} than for Cu^{2+}, Ni^{2+}, and Co^{2+}.
4. The APPA–NIPAAm (10:90) copolymer/metal (Sm^{3+}, Nd^{3+}, or La^{3+}) complexes became water-insoluble above 45°C at pH 6–7, but the APPA–NIPAAm (10:90) copolymer/metal (Cu^{2+}, Ni^{2+}, or Co^{2+}) complexes were water-soluble from 25 to 55°C at pH 6–7.

References

1. Fujishige, S.; Kubota, K.; Ando, I. J Phys Chem 1989, 93, 3311.
2. Baltes, T.; Fludy, F. G.; Freitag, R. J Polym Sci Part A: Polym Chem 1999, 37, 2977.

3. Zhang, X. Z.; Zhuo, R. X. Eur Polym J 2000, 36, 2301.
4. Berlinova, I. V.; Dimitrov, I. V.; Vladimov, N. G.; Samichkov, V.; Ivanov, Y. Polymer 2001, 42, 5963.
5. Tanaka, T. Phys Rev Lett 1978, 40, 820.
6. Tanaka, T. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1986; Vol. 6, p 514.
7. Freitas, R. F. S.; Cussler, E. L. Chem Eng Sci 1987, 42, 97.
8. Hoffman, A. S. J Controlled Release 1987, 4, 213.
9. Bae, Y. H.; Okano, T.; Hsu, R.; Kim, S. W. Macromol Chem Rapid Commun 1987, 8, 481.
10. Siegel, R. A.; Falamarzian, M.; Firestone, B. A.; Moxley, B. C. J Controlled Release 1988, 8, 179.
11. Siegel, R. A.; Firestone, B. A. Macromolecules 1988, 21, 3254.
12. Liu, H.; Avoce, D.; Song, Z.; Zhu, X. X. Macromol Rapid Commun 2001, 22, 675.
13. Kim, J.; Kim, J. Colloids Surf B 2002, 24, 45.
14. Guan, Y.; Ding, X.; Zhang, W.; Wan, G.; Peng, Y. Macromol Chem Phys 2002, 203, 900.
15. Ikehatam, A.; Ushiki, H. Polymer 2002, 43, 2089.
16. Watanabe, T.; Utsunomia, M.; Kurihara, S.; Nonaka, T. J Polym Sci Part A: Polym Chem 2001, 39, 1505.
17. Nonaka, T.; Hua, L.; Ogata, T.; Kurihara, S. J Appl Polym Sci 2003, 87, 386.
18. Eom, G. T.; Oh, S. Y.; Park, T. G. J Appl Polym Sci 1998 Part A: Polym Chem, 70, 1947.
19. Wohlrab, S.; Kuckling, D. J Polym Sci 2001, 39, 3797.
20. Research Groups of Microanalysis. Yuki Biryo Teiryo Bunseki; Nankodo: Tokyo, 1969; p 427.
21. Association of Japan Biochemistry. Shin Seikagaku Jikken Kouza; Tokyo Kagaku Dojin: Tokyo, 1990; Vol. 1, p 127.