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Formation of Thermosensitive Polymer Hydrogels by Crosslinking with Metal Ions and Their Functions

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Thermosensitive and water-soluble copolymers were prepared by copolymerization of acryloyloxypropyl phosphinic acid (APPA) and *N*-isopropyl acrylamide (NIPAAm). Thermosensitivity and metal adsorption ability of the copolymers were studied.
The APPA-NIPAAm copolymers having below 0.8 mmol/g of APPA moiety exhibited thermosensitivity around 40°C, but the APPA-NIPAAm copolymers having above 1.2 mmol/g of APPA moiety exhibited no thermosensitivity in the temperature range from 25°C to 55°C. The APPA-NIPAAm copolymers had higher adsorption capacity for Sm^{3+}, Nd^{3+}, or La^{3+} than for Cu^{2+}, Ni^{2+}, or Co^{2+}. The APPA-NIPAAm(10:90 mol ratio) copolymer-metal(Sm^{3+}, Nd^{3+}, or La^{3+}) complexes became water-insoluble at pH6-7 above 45°C, but the APPA-NIPAAm(10:90) copolymer-metal(Cu^{2+}, Ni^{2+}, or Co^{2+}) complexes were water-soluble at pH6-7 in the temperature range from 25°C to 55°C. The temperature at which these copolymer-metal complexes became water-insoluble shifted to higher temperature by increasing pH values of the solutions.

Keywords: Thermosensitive polymer, acryloyloxypropyl phosphinic acid, *N*-isopropylacrylamide, metal adsorption, polymer-metal complex

1. INTRODUCTION

We have been studying thermosensitive polymer hydrogels having antibacterial activity[1]. This report is concerned with the preparation of thermosensitive water-soluble polymers having adsorption ability for metal ions. The thermosensitive water-soluble polymers having adsorption ability for metal ions were prepared by copolymerization of acryloyloxypropyl phosphinic acid (APPA) and *N*-isopropylacrylamide (NIPAAm). The thermosensitivity and adsorption ability of APPA-NIPAAm copolymers obtained for metal ions such as Sm^{3+}, La^{3+}, Nd^{3+}, Cu^{2+}, Co^{2+} etc. were studied.

2.EXPERIMENT

2.1 Synthesis of water-soluble APPA-NIPAAm copolymers.

The structure of APPA-NIPAAm copolymers is shown in Fig.1. First, APPA and NIPAAm were dissolved in 20cm^3 of dimethylsulfoxide (DMSO) in a glass vessel under a nitrogen atmosphere. The copolymers were obtained by radical copolymerization using 2,2'-azobisisobutylonitrile as a radical initiator at 50°C for 1 h.

2.2 Measurement of phosphorous content in the APPA-NIPAAm copolymers.

The phosphonium content in the copolymers was calculated from the phosphorus content in the dried copolymers, which was determined by phosphovanadomolybdate method[2].

2.3 Measurement of thermosensitivity of APPA-NIPAAm copolymers.

The thermosensitivity of the APPA-NIPAAm copolymers was determined by measuring the transmittance of the copolymer solution at 660 nm at various temperatures.

2.4 Measurement of adsorption capacity for metal ions

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

3. RESULTS AND DISCUSSION

3.1 Synthesis of APPA-NIPAAm copolymers

The APPA-NIPAAm copolymers were obtained by copolymerization of APPA and NIPAAm in DMSO. The copolymers obtained were dissolved in deionized water and then purified by dialysis against deionized water. The copolymers were obtained by freeze drying.

Table I shows the phosphorous contents in APPA-NIPAAm copolymers obtained by varying the mol ratios of APPA and NIPAAm in feed from 3:97 to 40:60. These results indicate that the APPA-NIPAAm copolymers having various contents of phosphinic acid groups could be arbitrarily obtained by varying the APPA contents in feed.

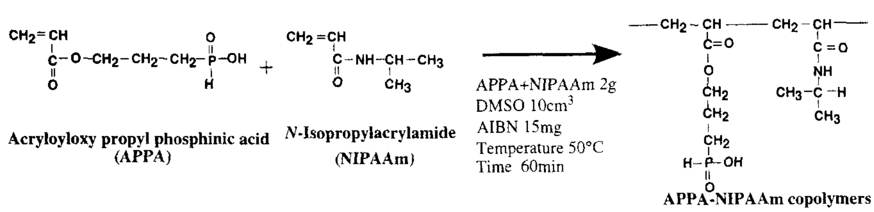

Fig.1 Synthesis of APPA-NIPAAm copolymers

Table I Content of phosphorus in APPA-NIPAAm copolymers

Component	Mol ratio in feed	P content Found. (wt%)	(mmol/g)	Calcd. (wt%)	(mmol/g)
APPA-NIPAAm	3:97	2.1	0.67	0.8	0.3
	5:95	2.2	0.70	1.3	0.4
	7:93	2.3	0.75	1.8	0.6
	10:90	2.5	0.8	2.6	0.8
	20:80	3.9	1.2	4.9	1.6
	30:70	5.0	1.6	7.0	2.3
	40:60	6.2	2.0	8.9	2.9

3.2 Thermosensitivity of APPA-NIPAAm copolymers

Thermosensitivity of APPA-NIPAAm copolymers was evaluated by measuring the transmittance at 660nm of the copolymer solutions of 5g/dm^3 at various temperatures. It is known that polyNIPAAm has a lower critical solution temperature (LCST). Therefore polyNIPAAm dissolves in water below 32°C, but indissolves above the temperature. The transmittance of solutions of APPA(<0.8 mmol/g)-NIPAAm copolymers decreased abruptly above 40°C, but the transmittance of solution of other APPA(>1.2mmol/g)-NIPAAm copolymers hardly decreased even by raising temperature above 40°C(Fig.2). This means that the introduction of much APPA into polyNIPAAm made the LCST of the APPA-NIPAAm copolymers above 55°C.

3.3 Effect of NaCl on thermosensitivity of APPA-NIPAAm copolymers

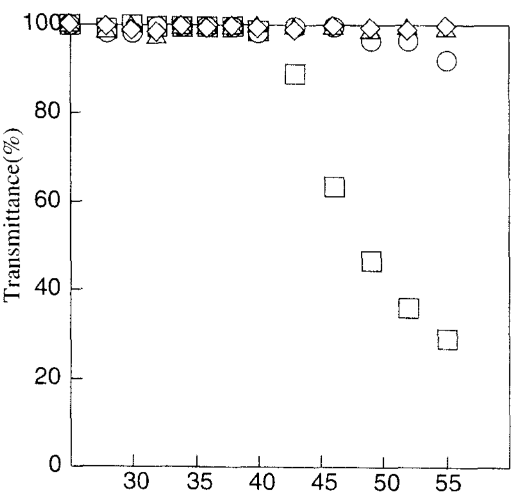

Fig.2 Temperature dependence of transmittance at 660nm of copolymer solutions

Concentration of copolymer solutions : 5g/dm^3

Copolymers:(□)APPA: NIPAAm = 10:90
(○)APPA: NIPAAm = 20:80
(△)APPA: NIPAAm = 30:70
(◇)APPA: NIPAAm = 40:60

The effect of addition of NaCl on the thermosensitivity of APPA-NIPAAm copolymers was measured in aqueous solutions. In the case of APPA-NIPAAm(3:97 and 7:93) copolymers, the transmittance of the copolymer solutions increased with increasing addition of NaCl in the concentration range up to 0.05 mol/dm^3. The reason for this increase is not clear at present. But, in the case of APPA-NIPAAm(20:80) copolymers, the transmittance of the copolymer solutions decreased by addition of NaCl.

Furthermore, in the case of APPA-NIPAAm(30:70 and 40:60) copolymers, the transmittance of copolymers hardly decreased even by addition of NaCl in the temperature range studied.

The high transmittance of the APPA(>30mol ratio)-NIPAAm copolymer solutions even by addition of NaCl up to 0.2 mol/dm can be explained by introduction of high content of APPA moiety into polyNIPAAm.

3.4 Adsorption ability of APPA-NIPAAm copolymers for metal ions

The adsorption ability of APPA(above 10 mol ratio)-NIPAAm copolymers for La^{3+} and Sm^{3+} was measured at various pHs. Fig.3 shows the results on Sm^{3+}. The adsorption capacity for Sm^{3+} increased with increasing pH of the solutions. Furthermore, the adsorption capacity for metal ions increased with increasing content of APPA moiety in the copolymers. The adsorption capacity of the copolymers for Cu^{2+},Co^{2+}, Ni^{2+} was also measured at various pHs. The order of adsorption capacity for metal ions is as follows:

Sm^{3+}, Nd^{3+}, La^{3+} > Cu^{2+}>Co^{2+}> Ni^{2+}.

That is, the APPA-NIPAAm copolymers have higher adsorption capacity for trivalent metal ions than divalent metal ions.

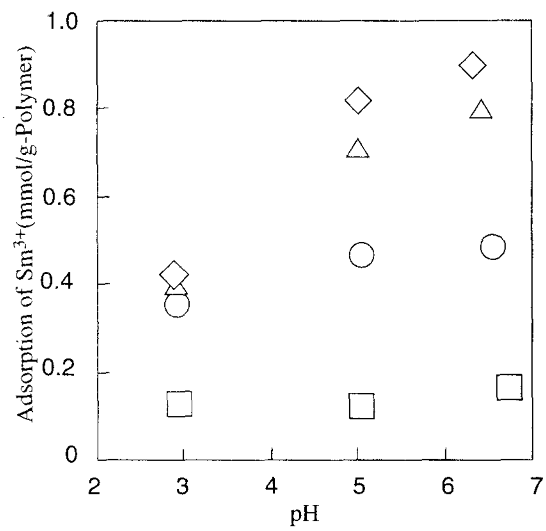

Fig.3 Effect of pH on the adsorption of Sm^{3+} with APPA-NIPAAm copolymers in the pH range from 3 to 7

Conditions;
Polymer solution (2.5g/dm^3) : 4cm^3
Metal ion solution (1.5×10^{-3}mol/dm^3) : 30cm^3
Buffer solution : CH_3COOH-CH_3COONa
Shaking at 30°C for 24hr

Copolymers:
(□)APPA:NIPAAm(10:90), (○)APPA:NIPAAm(20:80)
(△)APPA:NIPAAm(30:70), (◇)APPA:NIPAAm(40:60)

3.5 Thermosensitivity of APPA-NIPAAm copolymer-metal complexes

Thermosensitivity of APPA-NIPAAm(10:90) copolymer-metal complexes was evaluated by measuring the transmittance at 660nm of the copolymer-metal complex solutions at various temperatures. The transmittance of the copolymer-metal(La^{3+}, Nd^{3+},or Sm^{3+}) complex solutions decreased abruptly above 45°C and the transmittance became almost zero above 50°C (Fig.4).

The abrupt decrease in the transmittance of APPA-NIPAAm(10:90)-metal (La^{3+}, Nd^{3+},or Sm^{3+}) complex

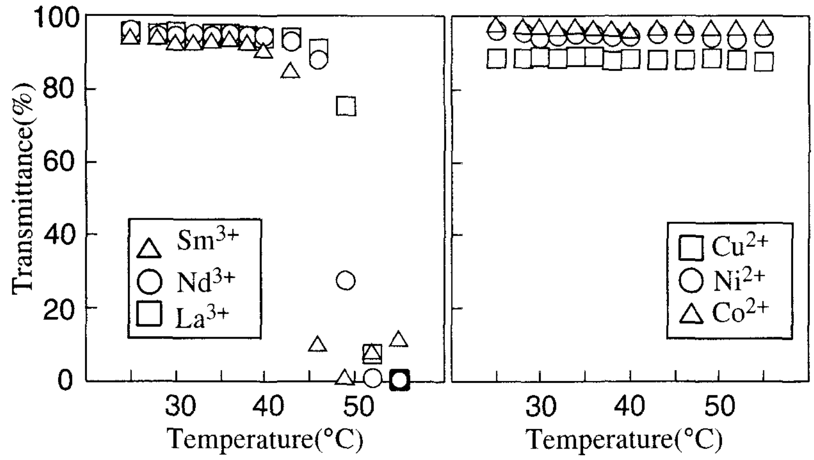

Fig.4 Temperature dependence of transmittance at 660nm of APPA-NIPAAm(10:90) copolymer-metal complex solutions at pH6-7

Concentration of copolymer : 2.5g/dm^3

Concentration of metal ion : 1.5 $\times 10^{-3}$ mol/dm^3

solutions in the temperature range studied indicates that the hydrophobic hydrogels were formed by crosslinking of copolymers with metal ions. On the other hand, the transmittance of the copolymer-metal (Cu^{2+}, Ni^{2+}, or Co^{2+})complex solutions hardly decreased in the temperature range studied.

The transmittance of APPA-NIPAAm-metal (La^{3+}, Nd^{3+}, or Sm^{3+}) complex solutions at 660nm 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 transmittance of APPA-NIPAAm (7:93) copolymer solution began to decrease above 37°C and it decreased to 50% at 50°C. However, for example, the transmittance of APPA-NIPAAm(7:93)-Sm^{3+} complex solution at pH3.5 began to decrease above 35 °C and it became almost zero at 38°C (Fig.5). The increase in the transmittance above 46°C with increasing temperature is due to the increase in the

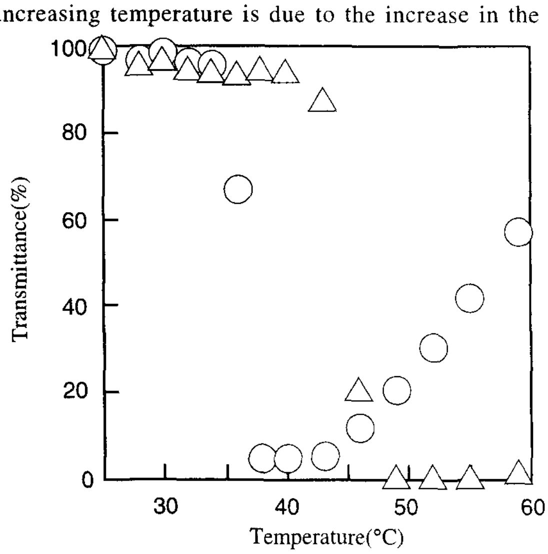

Fig.5 Temperature dependence of transmittane at 660nm of APPA-NIPAAm(7:93) copolymer-Sm^{3+} complex solutions at pH3.5 and pH6.5

Concentration of copolymer : 2.5g/dm^3

Metal ions / phosphonium groups in copolymer (mol ratio) = 6/1

pH:(○)pH3.5, (△)pH6.5

precipitates of copolymer-metal complexes with increasing temperature. On the other hand, at pH 6.5, the transmittance of the copolymer-Sm $^{3+}$complex solution decreased abruptly above 38°C and it became almost zero at 48°C. The similar phenomena were also observed in the case of copolymer-metal(La^{3+} or Nd^{3+}) complexes. This result indicates that the phase transition temperature at pH 6.5 shifted to higher temperature than that at pH3.5. The shift of transition temperature at higher pH to higher temperature is due to more dissociation of phosphinic acid groups at higher pH.

The abrupt decrease in transmittance of polymer-metal(La^{3+},Nd^{3+}, or Sm^{3+}) complex solutions is because the APPA-NIPAAm copolymer was crosslinked by metal ions and they became more hydrophobic hydrogels.

4. CONCLUSIONS

(1) Thermosensitive and water-soluble copolymers were prepared by copolymerization of APPA and NIPAAm.

(2) The APPA-NIPAAm copolymers having below 0.8 mmol/g of APPA moiety exhibited thermosensitivity around 40°C, but The APPA-NIPAAm copolymers having above 1.2 mmol/g of APPA moiety exhibited no thermosensitivity in the temperature range from 25°C to 55°C.

(3) The APPA-NIPAAm copolymers had higher adsorption capacity for Sm^{3+},Nd^{3+} or La^{3+} than for Cu^{2+}, Ni^{2+}, or Co^{2+}.

(4) The APPA-NIPAAm(10:90) copolymer-metal(Sm^{3+},Nd^{3+} or La^{3+}) complexes became water-insoluble at pH6-7 above 45°C, but the APPA-NIPAAm(10:90) copolymer-metal(Cu^{2+}, Ni^{2+} or Co^{2+}) complexes were water-soluble at pH6-7 in the temperature range from 25°C to 55°C

5. REFERENCES

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