Synthesis of Poly(acrylamide-*co*-4-vinylpyridine) Hydrogels and Their Application in Heavy Metal Removal

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ABSTRACT: A series of poly(acrylamide-*co*-4-vinylpyridine) hydrogels having varied acrylamide/4-vinylpyridine content and different crosslink ratios of *N,N'*-methylenebisacrylamide was prepared by using solution polymerization. The prepared hydrogel polymers were characterized by their elemental analysis, infrared spectroscopy, and equilibrium water content. The polymers were investigated toward metal ion uptake of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The polymers were more sensitive to Cu(II) and Ni(II) and the order of metal ion binding was Ni(II), Cu(II) > Zn(II) > Co(II) > Mn(II). Metal ion uptake by the polymers was reduced as the pH of the medium decreased. Recycling of the resins resulted in high recovery of the metal ions from their aqueous solutions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2522–2526, 2003

Key words: hydrogels; swelling; chelating polymers; heavy metals

INTRODUCTION

Polymer–metal complexes have become interesting for several research groups in recent decades due to their potential applications in several fields. They are applied in catalytic organic synthesis, enzyme-mimeting agents, wastewater treatment, drilling-mud additives, hydrometallurgy, and recovery of heavy and trace metal ions.[1–3]

A polymer ligand containing anchoring sites like nitrogen, oxygen, or sulfur is obtained either by polymerization of monomer possessing a coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability.[4] Various functional groups such as thiols, pyridine, 8-hydroxy-quinoline, polyamine, and glycol chains have been immobilized mainly on styrene–divinylbenzene copolymer, glycidylmethacrylate–divinylbenzene copolymer, phenol–formaldehyde resins, and cellulosic materials.[5–8]

Removal of metal ions from aqueous solution is a major industrial activity covering processes ranging from water softening to "leaching" of metals from ores to detoxification of wastewater and contaminated natural waters. Polymers containing appropriate ligand could provide a practical and economical means for removing dissolved metals present in parts per million (ppm) levels in wastewater and in organic media such as dodecane or jet fuels.[9] The methods of removing heavy metals from water include precipitation, ion-exchange, biosorption,[10] and reverse osmosis.[11]

Polyacrylamide (PAM) is highly hydrophilic polymer; it has served in wastewater treatment, papermaking industries, and agricultural applications for decades. On the other hand poly-4-vinylpyridine (P-4-VP) is less hydrophilic than polyacrylamide and is well known for its capability toward metal uptake.[12,13] Thus combination of both monomers in one polymer could lead to a new polymer with controlled hydrophile–lipophile balance and swelling properties that can be used for heavy metal removal, and catalytic and agricultural applications.

In this work, copolymers of acrylamide (AM) and 4-vinylpyridine (4-VP) in different mol ratios and different crosslink ratios of *N,N'*-methylenebisacrylamide (MBAM) were prepared by solution polymerization, and their swelling and metal uptake properties were investigated.

EXPERIMENTAL

Materials

Acrylamide (Merck) and MBAM were used as received. The 4-VP (Aldrich) was destilled under reduced pressure before use. Metal salts Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) were of reagent grade and used as received.

Preparation of crosslinked copolymers

Crosslinked copolymers of AM and 4-VP were prepared by using free radical solution polymerization

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TABLE I
Composition of Monomers and Yield for the Crosslinked
Acrylamide-*co*-4-vinylpyridine Copolymers

Sample	Composition (mol %)		MBAM (mol %)	Yield[a] (%)	DS[b]	EWC[c] (%)
	Acrylamide	4-VP				
1	49	49	2	83	4.55	89
2	65	33	2	88	5.60	92
3	33	65	2	79	3.15	86
4	47	47	6	84	4.17	90
5	63	31	6	85	5.13	91
6	31	63	6	81	2.55	84

[a] Based on weight of product to monomer weight.
[b] Degree of swelling, $DS = (P_w - P_d)/P_d$, where P_w is the weight of swollen polymer, and P_d is the weigh of the dry polymer.
[c] Equilibrium water content, $EWC = W_f \cdot 100$, where $W_f = (P_w - P_d)/P_w$.

according to standard procedure.[14] In a typical run for the synthesis of 2 mol % crosslinked 1:1 Am/4-VP copolymer; acrylamide 3.48 g (49 mol %) dissolved in 5 mL of methanol, MBAM 0.308 g (2 mol %) dissolved in 5 mL of methanol, and 4-VP 5.145 g (49 mol %) in 85 mL of toluene were placed in a 500 mL flask. The polymerization started by the addition of 5 mL of 1 wt % benzoylperoxide solution in toluene and the reaction mixture was heated at 80°C for 12 h. The solid polymer was filtered off, washed with methanol and diethylether, and dried at 50°C under vacuum for 24 h. Copolymers with 1:2 and 2:1 ratios of AM to 4-VP and 2–6 mol % crosslinking were prepared by varying the monomer composition in the feed (Table I). The prepared hydrogel polymers were characterized by their elemental analysis and Fourier transform infrared spectra (KBr) which showed absorptions at 3340 cm^{-1} (amide NH), 1645 cm^{-1} (amide C=O), 1590 cm^{-1} (CH=N pyridine unit), and at 2920 cm^{-1} (CH$_2$ chain).

Swelling of copolymers

The polymers (0.10 g) were swollen in water for 6 days and the degree of swelling was determined gravimetrically. The degree of swelling (SD) is given by SD $= (P_w - P_d)/P_d$, where P_w is the weight of swollen polymer, and P_d is the weight of the dry polymer. Equilibrium water content was calculated as EWC $= W_f \cdot 100$, where W_f is the weight fraction of water, and W_f is given as $W_f = (P_w - P_d)/P_w$, where P_w and P_d are defined as previously.

Metal complexation of the coplymers

Affinity of the chelating resins towards Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) metals is determined from batch equilibrium technique. Thus, a polymer (10 mmol) is shaken with 20 mL of the metal solution (5.0 × 10^{-3}N) for 48 h. The polymer is separated by filtration and the metal concentration in the solution is

measured by using atomic absorption spectrometry (Perkin Elmer 2380 atomic absorption spectrophotometer). For metal sorbing application at pH 4, nitric acid was used to adjust the pH.

Desorption and reuse

The metal-complexed polymers were freed from metals by treating with 1N HCl. The acid-treated polymers were filtered and washed with distilled water and bicarbonate solution to remove HCl. The filtrate was made neutral with drops of dilute NaOH. The concentration of desorebed metals was determined as previous. The desorption ratio was calculated as follows: desorption ratio = (Amount of metal ion desorbed into solution/Amount of metal ion bound to polymer) × 100. A second metal binding cycle was repeated with these regenerated resins.

RESULTS AND DISCUSSION

Synthesis of polymers

Copolymer hydrogels **1–6** of AM and 4-VP were prepared by free radical solution polymerization of the monomers in toluene at 80°C using benzoylperoxide as initiator. MBAM was used as crosslinking agent (Scheme 1). The products precipitate as polymerization proceed.

Actually, two groups of copolymers were prepared: The first one used 2 mol % of the crosslinker and the ratios of AM/4-VP were 1:1, 2:1, and 1:2 respectively, while the second group used 6 mol % of the crosslinker and the same ratios of AM/4-VP as previous. The composition of monomers and yield and other details for the synthesis of the chelating resins are given in Table I.

The obtained hydrogel polymers do not dissolve in water due to crosslinking but do take up water according to their composition. The hydrophilic nature of the hydrogel copolymer is enhanced by increasing
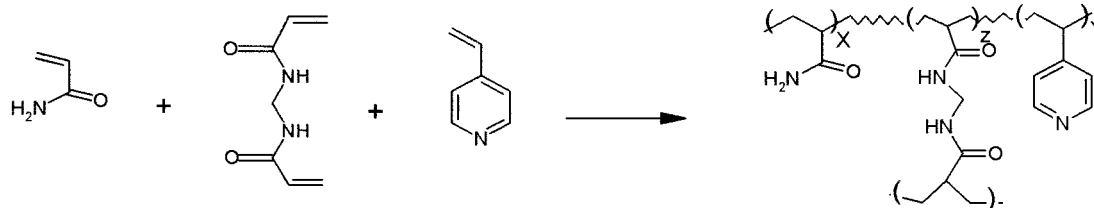
Polymer	X mol %	Y mol %	z mol %
1	49	49	2
2	65	33	2
3	33	65	2
4	47	47	6
5	63	31	6
6	31	63	6

Scheme 1 Preparation of AM/4-VP copolymers.

the amount of acrylamide. The equilibrium water uptake varied between 92% for hydrogel polymer **2**, having the highest amount of acrylamide and 84% for hydrogel polymer **6**, having the lowest amount of acrylamide. The increasing ratio of the crosslinking agent MBAM reduced the degree of swelling of the polymers especially polymers **3** and **6**, having the lowest amount of acrylamide. According to these results, swelling properties can be controlled by proper adjustment of the monomer composition. The polymers were prepared in this form to provide high surface area to facilitate their use in metal chelation, catalysis, and agricultural application as soil conditioners.

Removal of heavy metals

The uptake of heavy metals from aqueous solutions by the hydrogel copolymers was performed by the batch technique using a single solution of the metal ion of interest. The concentration of metal ion bound was calculated from the relation:

$$\text{Metal ion bound} = [(S_0 - S) \, V]/(W \times 1000) \quad (1)$$

S_0 and S represent the concentrations of the metal ion in aqueous solution (in mg/L) before and after interaction with polymers respectively. V is the volume (mL) of the aqueous phase and W is the amount (g) of the polymeric material used. The sorbing capacity of the investigated copolymers varied with composition of the hydrogel copolymers. The highest sorbing capacity observed for metal ions was for polymer **3.** The hydrogel copolymer **3** contains the largest amount of vinylpyridine where the ratio of AM/4-VP is 1:2 and the crosslink ratio was 2 mol. The efficiency of the hydrogels in metal ion uptake was in the order: **3** > **1** > **6** > **4** > **2, 5.** Copolymer **1,** having a 1:1 AM/4-VP ratio, was slightly more efficient in sorbing metals than copolymer **6,** having a 1:2 AM/4-VP ratio. However, copolymer **1** contains only 2 mol % crosslinker compared with 6 mol % crosslinker for copolymer **6.** The increased crosslink ratio probably makes metals

TABLE II
Capacities of Copolymeric Hydrogels for Metal Chelation

Sample	Metal ion uptake (mmol/g)[a]				
	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Co(II)
1	0.421	0.766	0.749	0.244	0.289
2	0.411	0.706	0.713	0.211	0.242
3	0.467	0.819	0.789	0.278	0.296
4	0.418	0.735	0.732	0.239	0.277
5	0.410	0.711	0.708	0.207	0.252
6	0.414	0.758	0.737	0.246	0.283

[a] Calculated from eq. (1).

TABLE III
Metal Chelation at pH 4[a]

Polymer	Metal ion uptake[b] (mmol/g)				
	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Co(II)
1	0.180	0.328	0.317	0.108	0.124
2	0.167	0.323	0.285	0.098	0.105

[a] Binding experiments were carried out in nitric acid (pH = 4).
[b] Calculated from eq. (1)

TABLE IV
Desorption of Metals

Polymer	Cu(II)	Desorption ratio[a] (%)	Mn(II)	Desorption ratio (%)
1	0.722	96.4	0.239	97.9
2	0.693	97.2	0.203	96.2
3	0.773	97.7	0.274	98.6
4	0.702	95.9	0.232	97.1
5	0.671	94.8	0.199	96.1
6	0.717	97.3	0.237	96.3

[a] Calculated as Desorption ratio = (Amount of metal ion desorbed into solution/Amount of metal ion bound to polymer) × 100.

less accessible to the chelating sites. Copolymers **2** and **5,** having the least amount of 4-VP (ratio of AM/4-VP is 2:1) were the least efficient in this series for metal binding.

It is obvious from these results that the amount of vinylpyridine and crosslinker control the binding capacity, since it is considered that the amide groups alone cannot form complexes with metal ions.[15] The results of Table II indicate that the order of metal binding for all polymers was Ni(II), Cu(II) > Zn(II) > Co(II) > Mn(II). These results are also in accordance with a previous study on Cu(II) chelation with polymers containing pyridyl and bipyridyl units in which these polymers were selective for Cu(II) over Co(II).[16]

Effect of low ph on chelating capacity

Hydrogel copolymers **1** and **2** were selected to study the role of lowering the pH on the chelating ability of the copolymers in presence of nitric acid (pH = 4). The hydrogels **1** and **2** have different vinylpyridine con-

tents, but the crosslink ratio is similar. Inspection of the results of Table III indicates that working at reduced pH resulted in reduction of the metal complexing ability of the hydrogel copolymers by ~42% compared with results previously listed in Table II. The reduced metal binding capacity of polymeric hydrogels **1** and **2** was systematic. The decrease in the chelating ability of the copolymers could be attributed to protonation of the pendant pyridine sites so that the metal ions could not interact easily with protonated pyridine units. These results are in accordance with previous results that showed great dependence on pH of the medium.[17–19]

Metal desorption and recycling

The capability of a polymer to be used in repeated operations is greatly influenced by its ability to easily desorb the bound metals under suitable conditions. With guidance from results of Table II, desorption of metals from copolymeric hydrogels using dilute HCl as desorbing agent was studied for Cu(II) and Mn(II), the most and least sorbed metals, respectively. The data presented in Table IV show that the desorption ratio was higher than 95%, which means that there is no difficulty in desorbing the metals from the copolymers, and both the strongly and weakly sorebed metals are easily removed by the dilute acid. The dilute acid used for desorption leads to breaking the coordination bonds between the metal ions and the pyridine sites and protonating the pyridine rings. Thus it leads to the release of the metals from polymers into solution.

Easy removal of metal ions from the polymer sites demonstrates that the approach may be extended for recycling of metal binding–desorption with the che-

TABLE V
Recycling Metal Binding

	(a) First recycle				
	Metals recycled[a] (mmol/g)				
Polymer	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Co(II)
1	0.391 (92.8%)[b]	0.712 (92.9%)	0.697 (93.1%)	0.226 (92.6%)	0.272 (94.0%)
4	0.391 (93.5%)	0.669 (91.0%)	0.676 (92.4%)	0.220 (92.1%)	0.253 (91.6%)
	(b) Second recycle				
	Metals Recycled[a] (mmol/g)				
Polymer	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Co(II)
1	0.387 (91.9%)[b]	0.706 (92.3%)	0.687 (91.7%)	0.225 (92.4%)	0.266 (92.3%)
4	0.393 (94.0%)[b]	0.672 (91.4%)	0.673 (91.9%)	0.222 (92.7%)	0.255 (92.1%)

[a] Calculated from eq. (1).
[b] Percent of recycled metal.

lating hydrogels. Hydrogel polymers **1** and **4** were selected for the recycling process. These copolymers have the same fraction of vinylpyridine, but they differ in their crosslink ratio. The two polymers **1** and **4** were chosen to study the applicability of the recycling process when the crosslink ratio is different. This process was repeated for two times from the single metal solution (Table V). The results of Table V indicate that metal rebinding capacity of the tested polymers for all metals did not change significantly through repeated applications compared with the first run (Table II). The higher ratio of the crosslinking agent present in polymer **4** did not affect the recycling progression.

CONCLUSIONS

New chelating hydrogel polymers containing varied AM/4-VP contents and different crosslink ratios were synthesized and examined for heavy metal removal from aqueous solutions. The amount of vinylpyridine present in the copolymer and crosslinker ratio controls the binding capacity of the copolymer. Working at low pH retards the chelating ability of the polymers. These polymers are suitable for multiple use in metal removal and can be applied for environmental cleanup. The results show that a polymeric material with specific swelling and chelating properties can be obtained by proper adjustment of the monomer composition to be used in a specific application.

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