

Ultrafiltration of Metal Ions by Water-Soluble Chelating Poly(*N*-acryloyl-*N*-methylpiperazine-*co*-*N*-acetyl- α -aminoacrylic acid)

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ABSTRACT: Water-soluble copolymers of *N*-acryloyl-*N*-methylpiperazine and *N*-acetyl- α -aminoacrylic acid were synthesized by radical polymerization. The copolymerization yield ranged between 60 and 97%. The FTIR and NMR spectra demonstrated that the copolymerization occurred. The copolymer composition was determined from $^1\text{H-NMR}$ spectra by comparison of methyl groups from both moieties. The copolymers were richest in AAA units. The metal ion retention properties were investigated by the liquid-phase polymer-based retention (LPR) technique at different pH and filtration factors. The affinity for the metal ions depended on the copolymer composition, pH, and filtration factor. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2556–2561, 2002

Key words: chelating polymers; ultrafiltration membranes; metal ions

INTRODUCTION

The increasing awareness of the environmental dangers posed by the discharge of toxic heavy metals into the environment and the accumulation of heavy metals in sewage sludge have resulted in progressively stricter legislation regarding effluent quality standards. With these more stringent standards, industries that previously discharged their effluent with minimal pretreatment are now being required to remove heavy metals down to very low concentrations.

Much of the theoretical work has been concerned with the removal of a metal cation that is

present as a single species. In reality, this ideal situation rarely exists and often the effluent contains a mixture of metals, a typical example of which would be the effluent derived from the electroplating industry.

Ultrafiltration (UF) and reverse osmosis have become standard procedures for the separation of heavy metal ions from aqueous solution. Because of the relatively large pore size of the membranes, UF/microfiltration has been used as a pretreatment method or as a means of recovering precipitated materials. Further, UF is used efficiently for product recovery and pollution control in the chemical and electronic as well as food and biotechnological industries.^{1–5}

Polymeric supports with complexing groups are widely investigated and applied for the metal recovery from a dilute solution, such as industrial fluids and wastewaters. Apart from insoluble, crosslinked polymer reagents,^{6–13} water-soluble chelating polymers, termed polychelatogens, have been investigated for the removal of metals in the

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homogeneous phase.^{14–22} By using these polychelatogens in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved. This method, based on the retention of certain metal ions by a membrane that separates low molar mass compounds from macromolecular complexes, is called liquid-phase polymer-based retention (LPR).^{14,18}

The aim of this study is to report the synthesis of a polychelatogen containing weak acid and tertiary amine moieties by radical copolymerization of *N*-acryloyl-*N*-methylpiperazine and *N*-acetyl- α -aminoacrylic acid and the investigation of their metal ion retention properties at different pH and filtration factor Z by using the LPR technique.

EXPERIMENTAL

Reagents

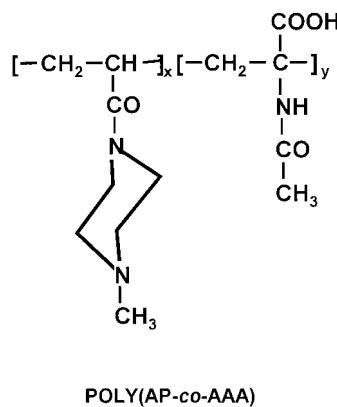
N-Acryloyl-*N*-methylpiperazine (AP) and *N*-acetyl- α -aminoacrylic acid (AAA) were synthesized and purified, respectively, according to the literature.^{23,24} AIBN was purified by recrystallization from methanol. The metal salts were commercially available and of analytical reagent grade. DMF was purified by the usual method.²⁵

Synthesis of the Water-Soluble Chelating Polymers

Three copolymers of AP and AAA were synthesized by radical solution (dimethylformamide [DMF]) polymerization using AIBN as initiator and varying the feed monomer ratio but keeping the total amount constant (0.04 mol). The polymers were purified and fractionated by ultrafiltration with a membrane with a molar mass cut-off (MMCO) of 100,000 g mol⁻¹. The polychelatogens were lyophilized and characterized by FTIR and NMR spectroscopy.

Ultrafiltration of the Metal Ions

For determination of the complexing binding ability, a 0.20 mM aqueous solution of polymer was prepared and adjusted to the corresponding pH by addition of diluted HNO₃ or NaOH. The solution of polychelatogen and metal nitrate (0.08 mM) were placed in the filtration cell. The total volume in the cell was kept constant at 20 mL. The system was pressurized by nitrogen gas and kept constant at 300 kPa during membrane filtration. A membrane with an exclusion rate of



POLY(AP-co-AAA)

Scheme 1 Poly(AP-co-AAA).

10,000 g mol⁻¹ was used. The filtration fraction ($Z = 1$ –10) was recollected and the concentration of metal ions in the filtrate was determined by atomic absorption spectroscopy. Z is defined as the ratio of the volume in the filtrate (V_f) and the volume in the cell (V_0).

Characterization

FTIR and NMR spectra were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Instruments, Madison, WI) and Bruker AC 250 multinucleus spectrometer (Bruker Instruments, Billerica, MA), respectively. The thermal properties were studied under nitrogen atmosphere by a Polymer Laboratories (UK) STA 625 thermal analyzer. The metal ions in the filtrate were determined with a Unicam Solar M Series flame and furnace atomic absorption spectrometer system (UK).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Water-Soluble Copolymers

Three copolymers of AP and AAA monomers by radical polymerization were synthesized by varying the feed monomer ratio and keeping the total amount (0.04 mol) constant (see **Scheme 1**). The copolymers were completely soluble in water. The yield increases as the AAA units increased from 60 to 97%. The yield is higher than that of the homopolymers (see Table I).

Among the most characteristic absorption bands the FTIR spectra show the following: 3342 cm⁻¹ (ν_{OH} carboxylic acid), 3300 cm⁻¹ ($\nu_{\text{N}-\text{H}}$ secondary amide), 2820 cm⁻¹ ($\nu_{\text{N}-\text{CH}_3}$), 1722 cm⁻¹

Table I Conditions and Results of Polymerization Reactions

Polymer Sample	Yield ^a (%)	Molar Ratio in the Feed AP : AAA	Copolymer Composition ^b AP : AAA
Poly(AP- <i>co</i> -AAA) ^c (2)	60	0.03 : 0.01	1.00 : 0.82
Poly(AP- <i>co</i> -AAA) ^c (3)	88	0.02 : 0.02	1.00 : 1.42
Poly(AP- <i>co</i> -AAA) ^c (4)	97	0.01 : 0.03	1.00 : 4.80
Poly(AAA)	60	—	—
Poly(AP)	65	—	—

T = 60°C; time 72 h.

^a After ultrafiltration by membrane with an exclusion limit of molecular weight of 10,000 Da.

^b It was determined by ¹H-NMR spectroscopy.

^c It was initiated by AIBN in DMF.

($\nu_{C=O}$ carboxylic acid), 1653 cm⁻¹ ($\nu_{C=O}$ secondary amide), 1360 cm⁻¹ (ν_{C-N}), and 1299 cm⁻¹ (ν_{C-O} carboxylic acid). The intensity of the signal placed at 1722 cm⁻¹ decreases as the content of the AAA units is decreased, and the intensity of the signal increases at 1657 cm⁻¹ as the content of the AP units is increased (see Fig. 1).

The ¹H-NMR spectrum shows the absorption signals corresponding to all proton types coming from both monomers (see Fig. 2). The absence of

vinyl proton absorption demonstrates that copolymerization occurred. The copolymer composition was determined by relating the integral area of the methyl protons of the AP with the area of all other protons (see Table I).

The copolymer structure was corroborated by ¹³C-NMR spectra showing the signals (δ in ppm) at 178 (C=O carboxylic acid), at 170 ppm (C=O amide), at 45 (CH₃—N), and at 22.6 (CH₃—CO).

The thermal stability studied under N₂ demonstrated that the copolymers were thermally stable up to 200°C with a weight loss lower than 15%.

Water-Soluble Copolymers/Metal Ion Interactions

The polymer fraction > 100,000 g mol⁻¹ was used to investigate the metal ion binding properties at

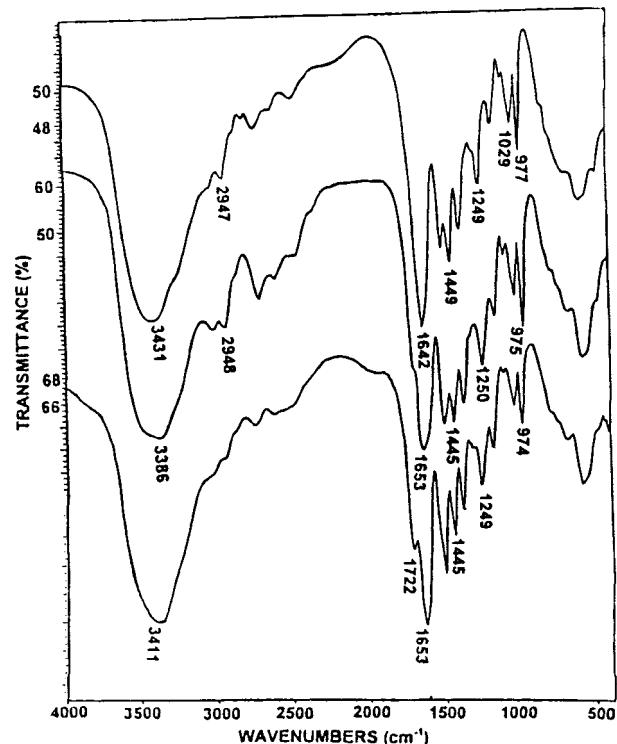
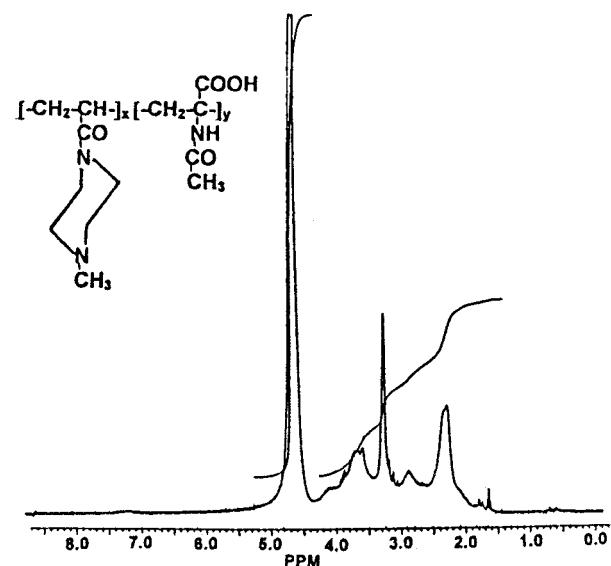


Figure 1 FTIR spectra of (a) poly(AP-*co*-AAA) sample 1; (b) poly(AP-*co*-AAA) sample 2, and (c) poly(AP-*co*-AAA) sample 3.



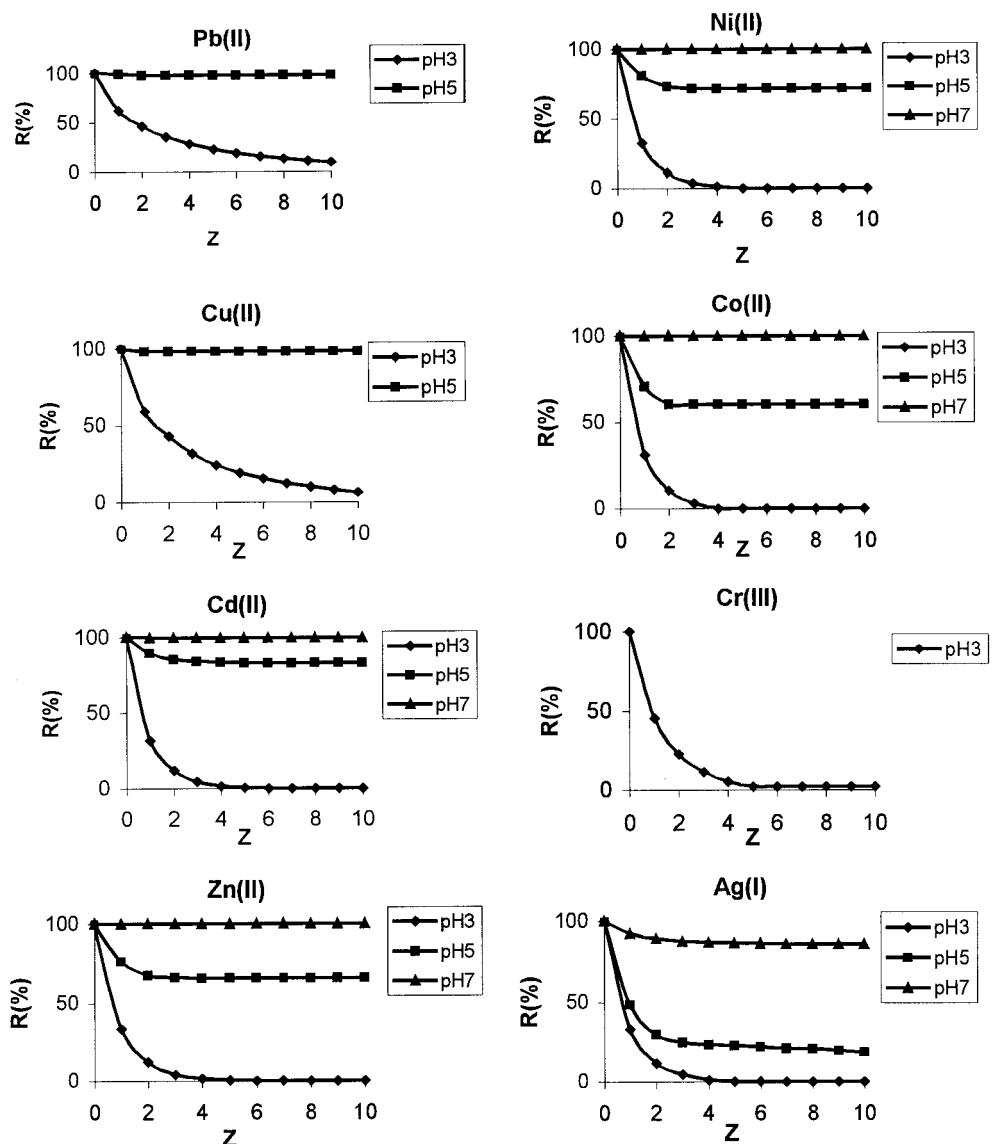


Figure 3 Retention profiles for the metal ions of poly(AP-co-AAA) sample 2 at different pH and Z values.

different pH and Z values. The ions were the following: Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III). In general, there is an effect of the pH on the retention properties. As the pH increases the affinity to the metal ions also increases. For all the copolymers, at pH 3 the retention affinity is very poor, such as at $Z = 2$, although it retains Cu(II) and Pb(II) in about 45%. However, the affinity for all the metal ions, except Ag(I), increases significantly at pH 5. Cr(III) ions were not investigated at pH > 3 to avoid the precipitation. The divalent cations Pb(II), Cu(II), Cd(II), Ni(II), Zn(II), and Co(II)

showed the highest retention. This behavior is slightly increased at pH 7 (see Fig. 3). This can be attributed to the strong participation of the carboxylate groups in the formation of polymer metal ion complexes. It is well known that these groups form stable mono- and bidentate complexes with divalent metal ions.²⁶

The effect of the copolymer composition on the metal ion retention was studied at $Z = 10$ and pH values of 3, 5, and 7. The results are summarized in Table II.

The copolymers with the highest content of AAA units showed the highest retention values at

Table II Effect of Copolymer Composition on the Metal Ion Retention at $Z = 10$ and pH 3, 5, and 7 for Poly(AP-*co*-AAA) System

Metal Ion	Copolymer Composition of Poly(AP- <i>co</i> -AAA)								
	1.00 : 4.80			1.00 : 1.42			1.00 : 0.82		
	pH 3	pH 5	pH 7	pH 3	pH 5	pH 7	pH 3	pH 5	pH 7
Ag(I)	1.9	76.8	97.7	0.0	18.4	85.8	0.0	3.9	34.7
Co(II)	0.0	98.6	100	0.0	60.2	100	0.0	0.0	97.0
Ni(II)	0.0	100	100	0.0	71.7	100	0.0	0.0	98.3
Cu(II)	0.0	100	—	6.0	98.2	—	7.0	47.8	—
Zn(II)	0.0	99.3	100	0.0	65.6	100	0.4	0.2	98.6
Cd(II)	0.0	99.6	100	0.0	83.0	99.5	0.2	0.6	99.5
Pb(II)	2.0	100	—	9.7	97.9	—	2.9	39.2	—
Cr(III)	4.6	—	—	0.0	—	—	10.5	—	—

pH 5 and 7. At these pH values the amino groups are deprotonated and the carboxylic groups remain as carboxylate, favoring the complex formation, because at lower pH the metal ions must compete with the protons.

The monovalent cation Ag(I) was retained significantly at pH 7. Thus, at this pH and $Z = 10$, the copolymer samples 1 and 2 retain 97.7 and 85.8%, respectively. Both copolymers are rich in AAA units, indicating that the carboxylate groups are strongly involved in the metal ion interactions.

CONCLUSIONS

Water-soluble copolymers by radical polymerization were obtained. The copolymerization yield and the copolymer composition depended on the feed monomer ratio. The highest yield value was achieved for the reaction with an excess of the AAA monomer unit in the feed. The AAA monomer showed a higher reactivity than AP monomer. Hence, the copolymers were richest in AAA units, except for that with an excess of AP unit in the feed.

The ability to bind metal ions also depended on the pH and copolymer composition. At higher pH the retention capability increased, which was attributed to the affinity of the carboxylate and tertiary amino groups to coordinate the metal ions. The copolymers with a higher content of AAA units showed a greater ability to interact with the metal ions, which demonstrated that the carboxylate groups form more stable complexes than the tertiary amino groups. The lower affinity

of the amino groups to bind metal ions should be attributed to the steric hindrance.

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REFERENCES

1. Strathman, H. *Sep Sci Technol* 1980, 15, 1135.
2. Johnson, A. S. *Desalination* 1970, 77, 135.
3. Erickson, A. *Desalination* 1985, 53, 259.
4. Michales, A. S. *Chem Eng Prog* 1968, 64, 31.
5. Molinari, R. *Membrane Technology: Applications to Industrial Wastewaters Treatment*; Kluver Academic: The Netherlands, 1995; p 101.
6. Ito, Y.; Saegusa, T. *J Macromol Sci Chem* 1979, A13, 523.
7. Berkel, P. M.; Driesse, W. L.; Reedijk, J.; Sherrington, D. C.; Zitsmanis, A. *React Funct Polym* 1995, 27, 15.
8. Beauvais, R. A.; Alexandratos, S. D. *React Polym* 1998, 36, 113.
9. Trochimczuk, A. W. *Eur Polym J* 1998, 34, 1047.
10. Bicak, N.; Scherrington, D. C.; Senkal, B. F. *React Funct Polym* 1999, 41, 69.
11. Rivas, B. L. in *The Polymeric Material Encyclopedia: Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996.
12. Rivas, B. L.; Maturana, H. A.; Ocampo, X.; Peric, I. M. *J Appl Polym Sci* 1995, 58, 2201.
13. Rivas, B. L.; Maturana, H. A.; Villegas, S. *J Appl Polym Sci* 2000, 77, 1994.
14. Geckeler, K. E.; Lange, G.; Eberhardt, H.; Bayer, E. *Pure Appl Chem* 1980, 52, 1883.

15. Geckeler, K. E.; Bayer, E.; Spivakov, B. Ya.; Shkinev, V. M.; Vorobeva, G. A. *Anal Chim Acta* 1986, 189, 285.
16. Spivakov, B. Ya.; Geckeler, K. E.; Bayer, E. *Nature* 1985, 315, 313.
17. Geckeler, K. E.; Shkinev, V. M.; Spivakov, B. Ya. *Sep Purif Methods* 1988, 17, 105.
18. Spivakov, B. Ya.; Shkinev, V. M.; Geckeler, K. E. *Pure Appl Chem* 1994, 66, 631.
19. Geckeler, K. E.; Zhou, R.; Fink, A.; Rivas, B. L. *J Appl Polym Sci* 1996, 60, 2191.
20. Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
21. Rivas, B. L.; Pereira, E. D. *Bol Soc Chil Quim* 2000, 45, 165.
22. Rivas, B. L.; Pereira, E.; Martinez, E.; Moreno-Viloslada, I. *Bol Soc Chil Quim* 2000, 45, 283.
23. Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2000, 21, 905.
24. Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2001, 22, 418.
25. Becker, H., et al. *Organikum*. VEB Deutscher Verlag der Wissenschaften: Berlin, 1972.
26. Pomogailo, A. D.; Dzhardimalieva, G. I. *Russ Chem Bull* 1998, 47, 2319.