

# Synthesis of Water-Soluble Polymers Containing Sulfonic Acid and Amine Moieties For the Recovery of Metal Ions Using Ultrafiltration

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Received 25 September 2000; accepted 13 January 2001

**ABSTRACT:** Copolymers from 2-acrylamido-2-methyl-propane sulfonic acid (APSA) and N-acryloyl-N-methyl piperazine (AP) were synthesized by radical polymerization with ammonium peroxydisulfate as the initiator. The copolymerization yield ranged between 93 and 95%. The copolymers were completely water soluble, and were characterized by FTIR and NMR spectroscopy. The copolymer composition was determined from elemental analysis through the S/C ratio. The binding capacity for metal ion was studied by the LPR technique at different pH and filtration factors. The retention depended strongly on the pH and on the copolymer composition. With increasing pH and increasing content of APSA units in the copolymer, the metal ion retention increased. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 22–30, 2001

**Key words:** water-soluble polymers; ultrafiltration membranes; metal ions; polymer-metal ion interactions

## INTRODUCTION

The continuous increase of world needs for most of the known metals, and the decrease in grade of the available ores, make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations.<sup>1–6</sup>

Heavy metal complexation by naturally occurring organic matter has been studied by many methods that have been extensively discussed.<sup>7,8</sup>

Unfortunately, all existing methods suffer from at least one of the following drawbacks:<sup>9</sup> poor sensitivity; adsorption of metal or organic matter to working surfaces; lengthy, repetitive procedures; inclusion of complexed metal in results for uncomplexed metal; lengthy and frequent calibration procedures; disruption of equilibrium conditions; restrictions to only a few metals; or restriction of working pH. Consequently, incomplete and incorrect data often are obtained with those methods.<sup>10–12</sup>

Membrane filtration processes can be successfully applied to the separation of inorganic species and for their enrichment from dilute solutions. More effective retention of certain metal ions and their enrichment and separation from other solutes by membrane filtration is achieved by using water-soluble polymers.<sup>13–18</sup>

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Correspondence to: B. L. Rivas.  
Contract grant sponsor: FONDECYT; contract grant number: 8990011.

Contract grant sponsor: Dirección de Investigación, Universidad de Concepción; contract grant number: 98.24.17-1.

*Journal of Applied Polymer Science*, Vol. 82, 22–30 (2001)  
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**Table I** Conditions and Results of Polymerization Reactions ( $T = 60^{\circ}\text{C}$ ; Time 24 h)

Polymer Sample	Yield <sup>a</sup> %	Mol Ratio in the Feed AP : APSA	Copolymer Composition <sup>c</sup> AP : APSA
Poly (AP) <sup>b</sup> (1)	59	—	—
Poly (AP-co-APSA) <sup>b</sup> (2)	93	0.03 : 0.01	1.00 : 0.40
Poly (AP-co-APSA) <sup>b</sup> (3)	95	0.02 : 0.02	1.00 : 0.95
Poly (AP-co-APSA) <sup>b</sup> (4)	97	0.01 : 0.03	1.00 : 2.40
Poly (APSA) <sup>b</sup> (5)	94	—	—

<sup>a</sup> After ultrafiltration by membrane with an exclusion limit of molecular weight of 100,000.

<sup>b</sup> It was initiated by ammonium persulfate in water.

<sup>c</sup> It was determined by elemental analysis.

Hydrophilic polymers with complexing groups (polychelatogens) have been tested to show the applicability of the method to the separation of various metal cations and anionic species for analytical and technical purposes. This method, based on the retention of certain metal ions by a membrane that separates low-molecular mass compounds from macromolecular complexes of the metal ions, is called Liquid-phase Polymer-based Retention (LPR).<sup>19,20</sup> A number of soluble and hydrophilic polymers with chelating groups have been prepared. A salient feature of these polychelatogens is their high solubility and hydrophilicity, which allows one to carry out the complexation in an aqueous phase.

This article reports the synthesis of copolymers containing strong acid and tertiary amine moieties such as 2-acrylamido-2-methyl-1-propane sulfonic acid and *N*-acryloyl-*N*-methyl piperazine, respectively, and their ability to bind metal ions by using the LPR technique.

## EXPERIMENTAL

### Reagents

2-Acrylamido-2-methyl-1-propane sulfonic acid (APSA) (Aldrich, Milwaukee, WI) was purified by distillation. *N*-acryloyl-*N*-methyl piperazine (AP) was synthesized according to the literature<sup>21</sup> (yield 65%). Ammonium peroxydisulfate and the metal salts (Merck, analytical grade) were used as received.

### Synthesis of the Polychelatogens

Three different monomer ratios of APSA and AP were polymerized in distilled water (100 mL) with ammonium peroxydisulfate (APS, 2 mol %) as the

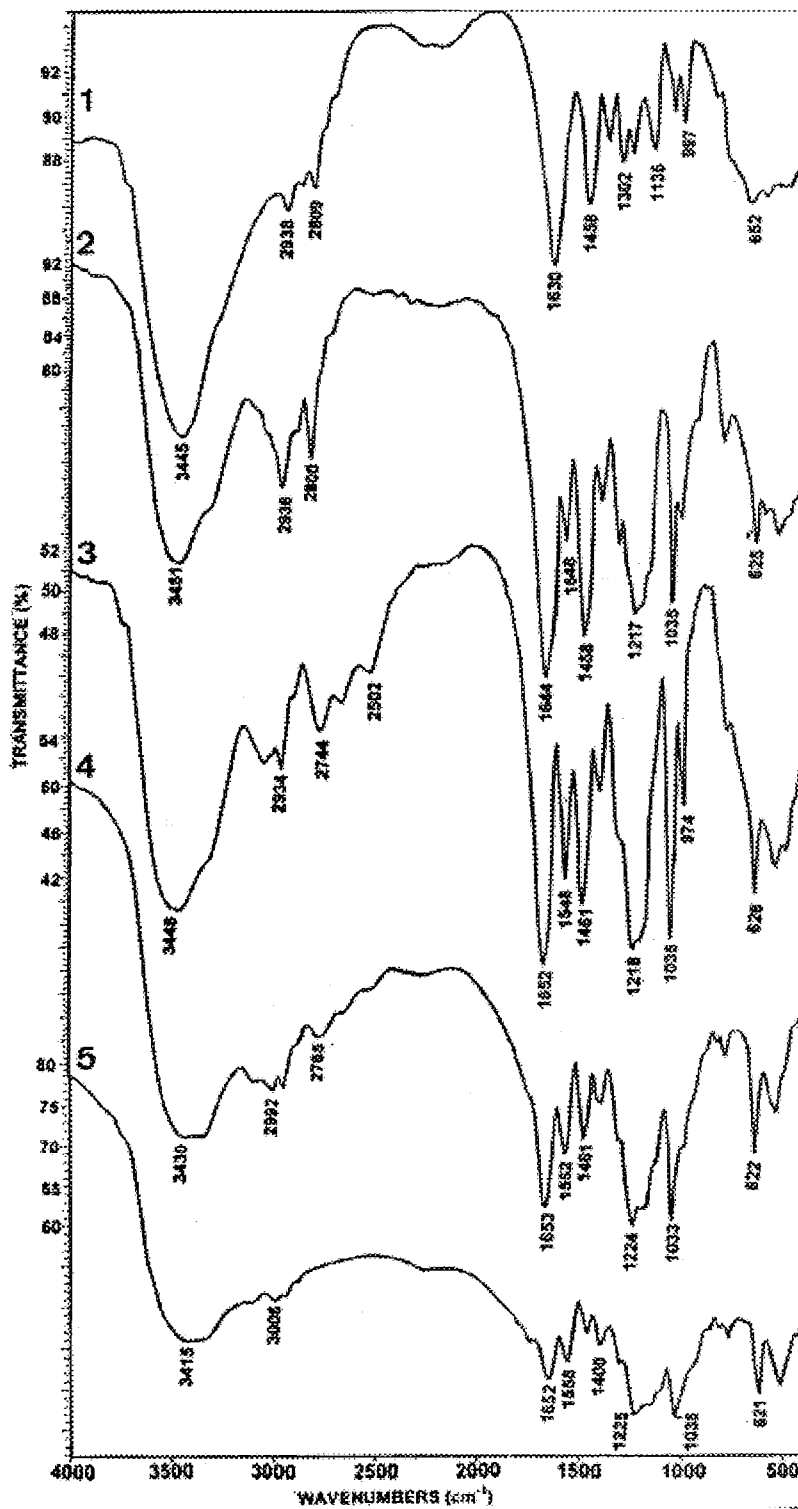
initiator at 60°C for 24 h, while keeping the total amount (0.04 mol) constant. The copolymers were purified and fractionated by using membranes with a molar mass cutoff (MMCO) of 100,000 and 50,000 g mol<sup>-1</sup>. Fractions of <50,000 g mol<sup>-1</sup> were not obtained. The products were lyophilized, dried under vacuum up to constant mass, and characterized by FTIR and NMR spectroscopy. The homopolymers were analogously synthesized by radical polymerization.

### Polymer–Metal Ion Binding Studies

The polymers (0.25 mmol, molecular mass fraction >100,000 g mol<sup>-1</sup>) were dissolved in bidistilled water, and the metal solutions (20 ppm of each metal) were added. The ratio of metal ion to polymer repeat unit was 40. The solution volume was brought to a total volume of 20 mL and the pH was adjusted to the defined value. The filtration runs were carried out using membranes with an MMCO of 10,000 g mol<sup>-1</sup> with a pressure of 300 kPa, while keeping the total volume in the cell constant at 20 mL. Filtration fractions were continuously collected and the metal ions concentrations analyzed by atomic absorption spectroscopy (AAS). The metal ions Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III) were investigated.

### Analytical Methods

The FTIR and NMR spectra were recorded on a Magna Nicolet 550 spectrophotometer and Multi-nucleous Bruker AC 250 P spectrometer, respectively. The metal ion binding studies were carried with a membrane filtration equipment, which has been described previously.<sup>19</sup> The membrane filtration consisted of a membrane filtration cell containing the polychelatogen solution, to which the solutions of metal ions were added under stir-

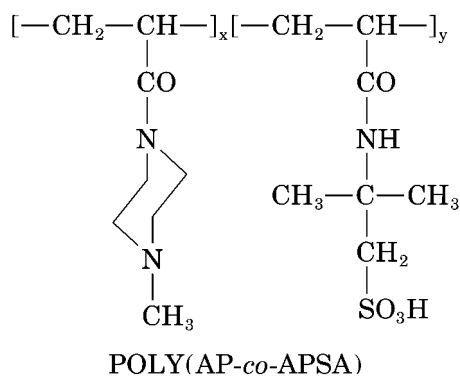


**Figure 1** FTIR spectra of (1) poly(AP), (2) poly(AP-co-APSA), sample 2, (3) poly(AP-co-APSA), sample 3, (4) poly(AP-co-APSA), sample 4, and (5) poly(APSA).

ring. For the separation, the washing solution was passed to the cell from the reservoir. Metal ion analysis was conducted on a Perkin-Elmer 3100 atomic absorption spectrometer. The thermal properties were studied with a Polymer Laboratories STA 625 Thermal Analyzer under nitrogen.

## RESULTS AND DISCUSSION

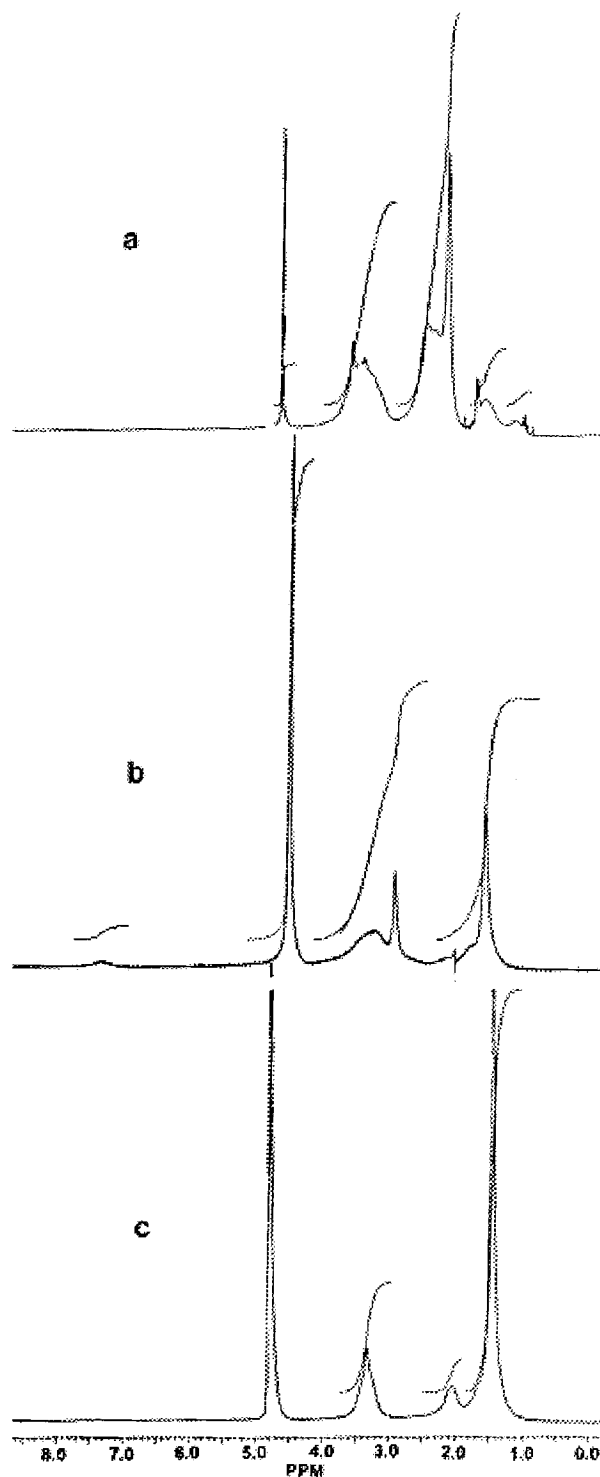
To obtain water-soluble polymers containing ligands and ion exchange groups, solution polymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA) and *N*-acryloyl-*N*-methyl piperazine (AP) was carried out at different feed compositions, but keeping the total amount of substance constant (0.04 mol) (see Table I). The homopolymers were also synthesized analogously to compare the metal ion retention ability (see Table I).



The yield of copolymerization varied between 93 and 95%, and did not depend on the feed monomer ratio.

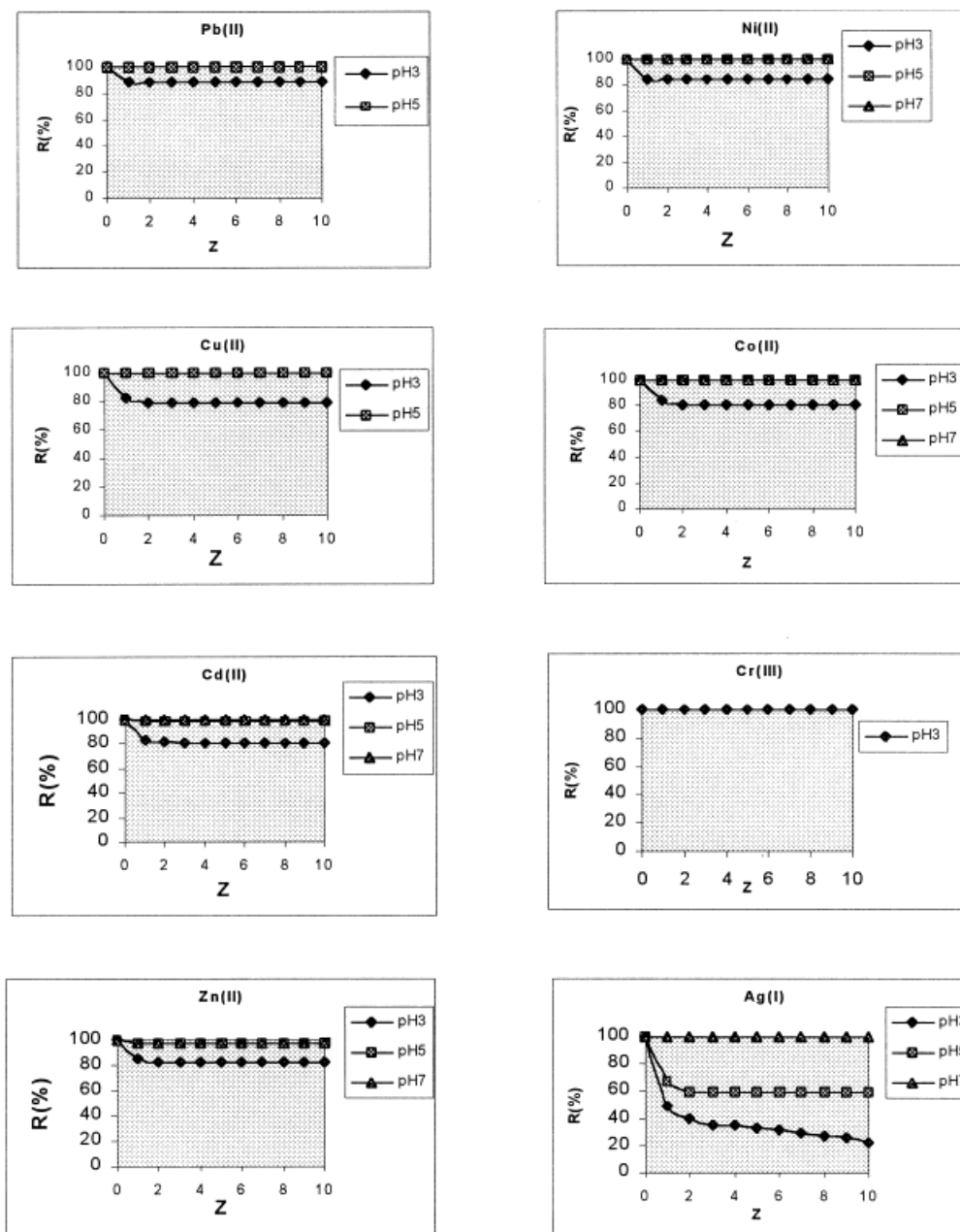
The FTIR spectra of the copolymers show basically the same pattern with mean absorption bands at 1644–1653  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$  amide), 622–625  $\text{cm}^{-1}$  ( $\nu_{\text{C}-\text{S}}$ ), 1458–1461  $\text{cm}^{-1}$  ( $\nu_{\text{C}-\text{N}}$ ), and 1217–1224  $\text{cm}^{-1}$  ( $\nu_{\text{S}-\text{O}}$ ). The signal intensity at 1458–1461  $\text{cm}^{-1}$  decreases with the decrease of the content of AP units as well as the signal intensity at 1217–1224  $\text{cm}^{-1}$  increased with an increase of the content of APSA units (see Fig. 1).

The  $^1\text{H-NMR}$  spectra of the copolymer and both homopolymers are shown in Figure 2. The assignment of the absorption signals was performed considering characteristic signals of analog low-molecular compounds.<sup>22,23</sup> The signal at 4.9 ppm corresponds to  $\text{D}_2\text{O}$  (99.9%). The signal registered at 3.2–3.6 ppm is attributed to methylene protons linked to sulfonic acid group. There is no absorp-



**Figure 2**  $^1\text{H-NMR}$  spectra (250 MHz,  $\text{D}_2\text{O}$  99.9%, room temperature) of (a) poly(AP), (b) poly(AP-co-APSA), sample 3, and (c) poly(APSA).

tion signal in the region corresponding to the vinyl protons which corroborates that the copolymerization occurred. All the  $^{13}\text{C-NMR}$  spectra



**Figure 3** Retention of metal ions in an aqueous solution of poly(AP-co-APSA), sample 2, as a function of the ratio of filtrate volume to cell solution volume ( $Z$ ) at pH 1, 3, 5, and 7.

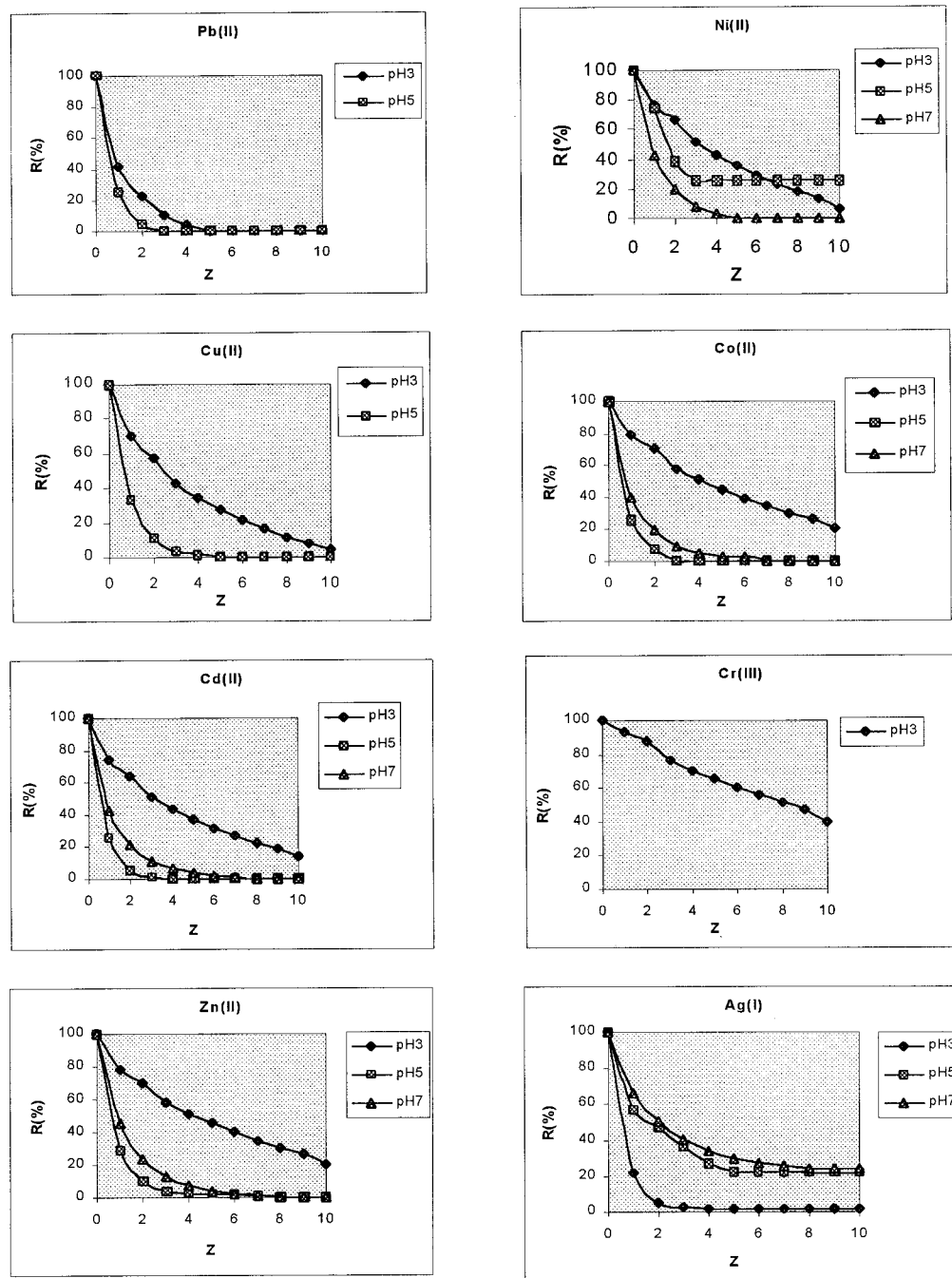
show the absorption signals, particularly at 180 ppm, assigned to amide carbonyl carbon, which corroborate the copolymer structure and that radical copolymerization occurred through the double bonds.

As the type of protons stemming from both monomers absorbed in a similar region, it was not possible to determine the copolymer composition by comparison of the proton integration areas.

Therefore, it was calculated from elemental analysis through the S/C ratio. The copolymers are richer in APSA units, due to the higher reactivity of the APSA radical than that of the AP radical.

The thermal stability of the copolymers studied under nitrogen shows that the copolymer are stable up to 200°C, showing a weight-loss lower than 10%.

The metal ion binding properties of the water-soluble poly(APA-co-AP) were investigated by

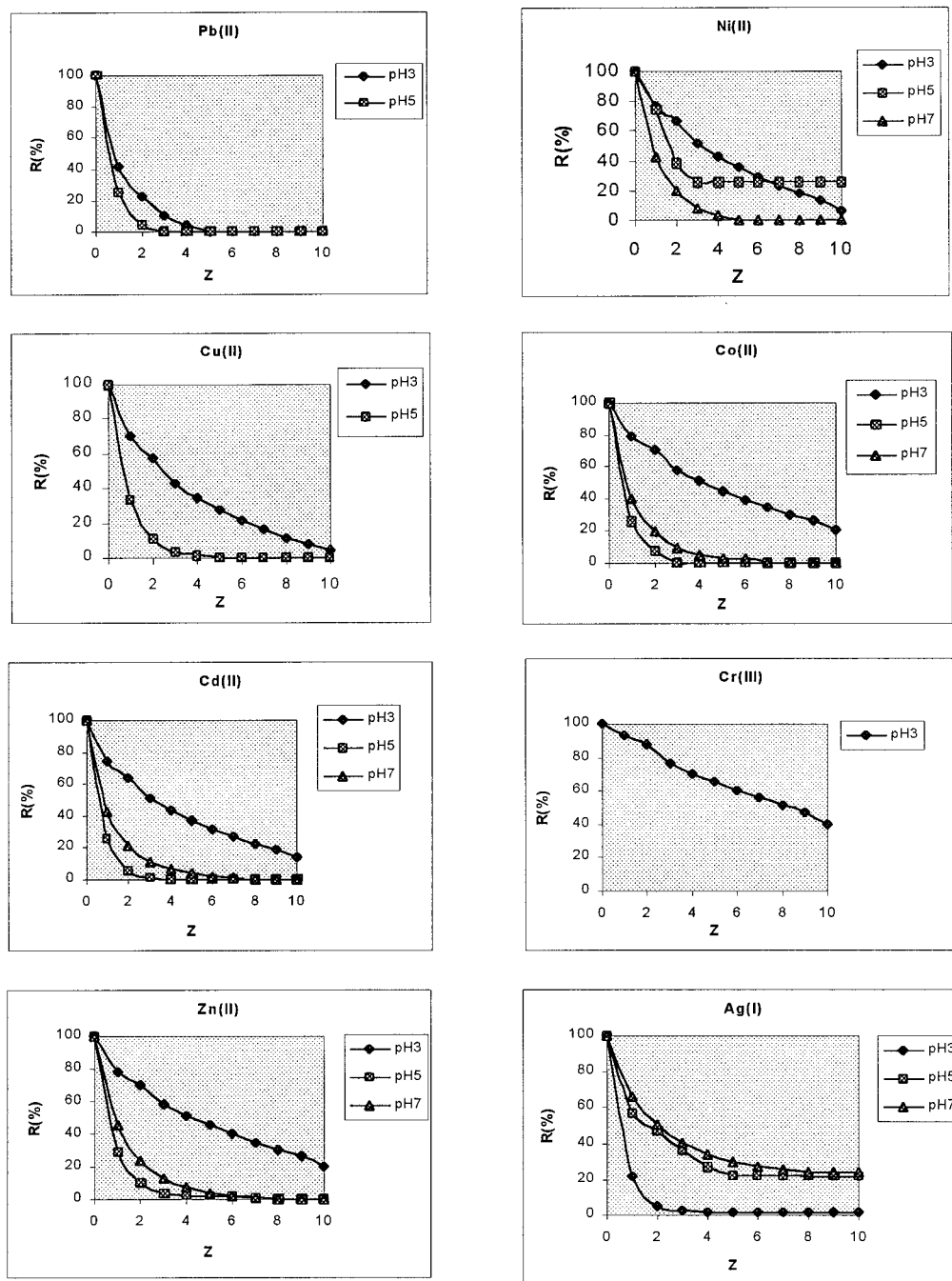


**Figure 4** Retention of metal ions in an aqueous solution of poly(AP-co-APSA), sample 3, as a function of the ratio of filtrate volume to cell solution volume ( $Z$ ) at pH 1, 3, 5, and 7.

means of LPR. Both homopolymers poly(APSA) and poly(AP) were also studied for comparison. The polymer fraction of  $>100,000 \text{ g mol}^{-1}$  was obtained by using filtration membranes with this MMCO. Typical retention profiles were obtained, by plotting the retention  $R$  vs. the filtration factor

$Z$ , and they are shown in Figs. 3–5.  $Z$  is defined as the ratio of the volume of filtrate  $V_f$  and the volume of cell solution  $V_o$ .

There is an important effect of the pH and the copolymer composition on the metal ion binding. As the content of the APSA units is increased, the



**Figure 5** Retention of metal ions in an aqueous solution of poly(AP-co-APSA), sample 4, as a function of the ratio of filtrate volume to cell solution volume ( $Z$ ) at pH 1, 3, 5, and 7.

metal ion retention increased. Those copolymers with a higher content of AP units show a lower affinity to bind metal ions. This effect was observed practically at all pH values. The tertiary amino groups would be hindered to interact with the ions due to the steric effect of the heterocyclic

ring. Only Cr(III) is retained significantly (60% at  $Z = 5$ ). The P(APSA-co-AP) sample 3 forms more stable complexes at pH = 5.0 and 7.0, except for Cr(III) at pH = 3. That is, Pb(II), Cu(II), Cd(II), Zn(II), Ni(II), Co(II), 100% at pH = 5.0 and Ag(I) 100% at pH = 7.0. These values are higher than

**Table II Metal Ion Retention Capacity C mmol of Metal Ion/g of Polymer (at Z = 5 pH = 5)**

Metal Ion <sup>a</sup>	C				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Ag(I)	0.0543	0.0178	0.0244	0.0599	0.0479
Co(II)	0.1383	0	0.0214	0.0795	0.1213
Ni(II)	0.1359	0.0560	0.0131	0.0772	0.1194
Cu(II)	0.1081	0.0128	0.0327	0.0811	0.1254
Zn(II)	0.1359	0	0.0222	0.0775	0.1195
Cd(II)	0.1290	0	0.0232	0.0770	0.1184
Pb(II)	0.0489	0.0510	0.0314	0.0776	—

<sup>a</sup> Initial mmol of each one in the cell:  $5 \times 10^{-3}$ .

those of both homopolymers poly(APSA) and poly(AP). This behavior is attributed primarily to the interaction of the metal ions with the sulfonic acid groups, basically by electrostatic interactions through the sulfonate groups, which is favored by the pH. Copper(II) was not investigated at higher pH due to the formation of a colloidal gel.

We have been interested to determine the retention behavior after a number of cycles at a pH where the retention is high. Accordingly, the metal binding capacities (mmol of metal ion per g of polychelator) of all polychelators were determined at pH = 5 and Z = 5. The results are summarized in Table II. In general, the copolymers (samples 2, 3, and 4), showed an increasing capacity as the APSA units content increased. The capacity values of the copolymer sample 4 are similar to those of the both homopolymers (samples 1 and 5). The copolymer sample 4 had the highest content of APSA units and shows a high

capacity (0.0599 mmol/g of polymer) for silver ions. The copolymer sample 2 shows also a relatively high capacity for Ni(II) (0.056 mmol/g of the polymer) and Pb(II) (0.0510 mmol/g of polymer). On the other hand it shows a good selectivity, as did not retain Co(II), Zn(II), and Cd(II) ions.

The polymer-metal interactions were very stable, indicated by constant retention of the copolymer at Z = 10 (Table III). When comparing the metal ion binding ability of the homopolymers, poly(AP) shows a low retention at pH 1, which increased at pH = 3 for Co(II), Ni(II), Zn(II). In this case, polymer-metal ion complexation occurred involving the tertiary amino groups. On the other hand, poly(APSA) shows a high affinity to bind metal ions, except for Ag(I), which is practically independent of the pH. The low retention of Ag(I) can be explained by the lower charge, leading to smaller electrostatic interactions. The copolymers also show a dependency of the copol-

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

Metal Ion	Copolymer Composition of Poly(AP-co-APSA)										
	Poly(AP)			1.00 : 2.44			1.00 : 0.95			1.00 : 0.40	
	pH3	pH5	pH7	pH3	pH5	pH7	pH3	pH5	pH7	pH3	pH5
Ag(I)	2.6	19.3	9.6	22.6	59.4	100.0	6.6	9.8	7.8	1.6	22.2
Co(II)	11.8	61.7	0.52	80.0	100.0	100.0	0.0	9.5	0.0	20.5	0.0
Ni(II)	11.9	66.0	2.4	83.6	100.0	100.0	0.0	9.8	0.0	5.7	25.4
Cu(II)	8.3	24.7	—	79.3	100.0	—	0.0	23.5	—	4.1	0.0
Zn(II)	13.1	59.5	1.8	81.9	97.8	98.0	1.8	14.0	1.1	20.3	1.4
Cd(II)	7.5	47.8	0.0	80.5	98.2	100.0	0.3	16.6	0.3	13.9	0.0
Pb(II)	0.5	5.0	—	88.5	100.0	—	0.0	29.4	—	0.0	0.0
Cr(III)	49.7	—	—	100.0	—	—	9.1	—	—	39.4	—



mer composition on the retention. Thus, the poly(APSA-co-AP) with the highest content of APSA units showed the highest degree of stable polymer-metal ion interactions, which increased with increasing pH. The increase of the retention of Ag(I) from 59.4% at pH = 5 to 100% at pH = 7 is noteworthy, that could be attributed to a synergistic effect (see Table II). This behavior has been also previously reported for other polychelators.<sup>24</sup>

## CONCLUSIONS

Water-soluble copolymers containing sulfonic acid and tertiary amine groups were synthesized by radical copolymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid and *N*-acryloyl-*N*-methyl piperazine. The sulfonic acid units dominated in the copolymer composition. The metal ion binding affinity strongly depended on the copolymer composition and the pH. With increasing content of sulfonic acid moieties the affinity for metal ion binding increased. The copolymer with the highest content of sulfonic acid showed the highest affinity to Ag(I), comparable to both homopolymers. The copolymer with the highest content of *N*-acryloyl-*N*-methyl piperazine units showed a high selectivity for Ni(II) and did not retain Co(II), Zn(II), and Cd(II), when compared with the other copolymers and the homopolymers.

With increasing the pH, the metal ion retention increased due to the deprotonation of the tertiary amino and sulfonic groups, thus favoring the interaction with the metal ions.

The authors thank FONDECYT (No. 8990011) and Dirección de Investigación, Universidad de Concepción (No. 98.24.17-1).

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