# Novel Water-Soluble Acryloylmorpholine Copolymers: Synthesis, Characterization, and Metal Ion Binding Properties

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**ABSTRACT:** Poly(4-acryloylmorpholine), poly(4-acryloyl-morpholine-co-2-acrylamido-2-methyl-1-propane sulfonic acid), and poly(2-acrylamido-2-methyl-1-propane sulfonic acid) were synthesized by radical polymerization. The water-soluble polymers obtained, containing tertiary amino, amide, and sulfonic acid groups, were investigated, in view of their metal binding properties, as polychelatogens by using the liquid-phase polymer-based retention technique, under different experimental conditions. The metal ions investigated were Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Pb(II), Zn(II), Cr(III), and Al(III). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 180–185, 2006

**Key words:** acryloylmorpholine polymers; water-soluble polymers, metal–polymer complex; metal ions; membranes

## INTRODUCTION

Polymeric supports with complexing groups are widely investigated and applied for the metal recovery from dilute solutions, such as industrial fluids and waste waters. The interest in the use of water-soluble polymers (WSPs) in conjunction with ultrafiltration membranes, to separate metal ions from aqueous solutions, has steadily grown since the early 1980s. The possibility of synthesizing derivatives of commercially available WSPs to achieve selective metal ion complexation has been recognized from early on. Thus, water-soluble functional polymers containing ligands, on the main or side chains, have been investigated for the removal of metal ions in the homogeneous phase.[1–24] These chelating polymers, termed polychelatogens, have been prepared, by functionalizing various functional polymers. Hydrophilic polymers with complexing groups have been tested, to show the applicability of the method, for the separation of various metal cations for analytical and technological purposes. This method, the liquid-phase polymer-based retention (LPR), is based on the retention of certain ions by a membrane, which separates low molecular mass compounds from macromolecular complexes of the ions.[8–11] Thus, uncomplexed inorganic ions can be removed with the filtrate, whereas the WSP complexes are retained. WSPs are commercially available or can be synthesized by different routes. Among the most important requirements for technological applications of these polymers, their high solubility in water, easy and cheap route of synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, high affinity to one or more metal ions, and selectivity for the metal ion are of interest. These ligands are attached to the backbone or at the side chain, either directly or through spacer groups. Using these polychelatogens in combination with membrane filtration, a higher efficiency and selectivity of membrane separations can be achieved.

To achieve enrichment of the metal ions, their solution can be passed from a reservoir to a smaller volume filtration unit, in the presence of a complexing polymer. This concentration method (enrichment method) is designed for metal recovery from dilute technological solutions and for absolute preconcentration of elements in analytical chemistry. However, interfering components of the test solution remain partly in the cell after the filtration run, even if they do not interact with the reagent. This can cause difficulties, for example, in trace analysis of highly mineralized waters. To avoid this, a combined procedure is applied to both absolute and relative preconcentrations.

Therefore, the aim of this article is to study the metal ion retention properties of WSPs, containing

amine, amide, and sulfonic acid moieties, based on poly(4-acryloylmorpholine) P(AcMo) through the LPR technique, under different experimental conditions.

## EXPERIMENTAL

### Reagents

4-Acryloylmorpholine (AcMo, 97%; Aldrich, Milwaukee, WI) was purified by distillation. Acrylamide (AAm, 99%; Fluka, Basel, Switzerland) was purified by recrystallization from methanol. 2-Acrylamido-2-methyl-1-propane sulfonic acid (APSA, 99%; Merck, Stuttgart, Germany) was used as received, without further purification.

The metal nitrates Ag(I), Cd(II), Cu(II), Ni(II), Co(II), Pb(II), Zn(II), Cr(III), and Al(III) (Merck, analytical grade, solution 1000 mg/mL) were used as received.

### Synthesis of the polychelatogens

P(AcMo) was synthesized by radical polymerization, using 5.648 g (0.04 mol) of AcMo. Ammonium persulfate (AP; 0.1–5 mol %) was added, and the flask was kept at 60°C for 24 h. After that, the polymer was lyophilized.

Yield: 99%. FT-IR spectrum (KBr, pellet) shows the following characteristic absorption signals: C—C (2919 cm$^{-1}$), O—CH$_2$ (2857 cm$^{-1}$), C=O (1639 cm$^{-1}$), —CH$_2$— (1447 cm$^{-1}$), and O—C—O (1113 cm$^{-1}$). $^1$H NMR spectrum (250 MHz, D$_2$O, 29°C, TMS as internal standard) shows the following signals: —CH— and —CH$_2$— (between 1.38 and 1.73 ppm), —CH$_2$—CH(C=O) (2.68 ppm), CH$_2$—N—CH$_2$—, and CH$_2$—O—CH$_2$ (between 3.4 and 3.8 ppm). $^{13}$C NMR spectrum (250 MHz, D$_2$O, 29°C, TMS as internal standard) shows the presence of the following carbons: —CH$_2$—CH— (39 ppm), —CH—C=O (59 ppm), —CH$_2$—N—CH$_2$— (65.5 ppm), —CH$_2$—O—CH$_2$— (69 ppm), and C=O (180 ppm).

P(AcMo-co-AAm) copolymerization reaction was carried out by an equimolar feed ratio of AcMo and AAm. To this, 0.045 mol of AcMo (6.350 g) and 0.045 mol of AAm (3.200 g) were added to the copolymerization flask. The initiator AP (1 mol %, 0.0009 mol, 0.205 g) was added, and the reaction was kept at 60°C for 24 h. After this, the polymer was lyophilized.

Yield: 98%. FT-IR spectrum (KBr pellets) shows absorption bands as follows: C—C (2931 cm$^{-1}$), O—CH$_2$ (2859 cm$^{-1}$), C=O (1629 cm$^{-1}$), and O—C—O (1110 cm$^{-1}$). $^1$H NMR spectrum (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the following signals: —CH$_3$ and —CH$_2$— (between 1.40 and 1.52 ppm), —CH— (3.1 ppm), CH$_2$—N—CH$_2$— and —CH$_2$—O—CH$_2$— (between 3.4 and 3.7 ppm). $^{13}$C NMR (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the presence of the following carbons: —CH$_3$ (27 ppm), —CH$_2$—CH— (38

ppm), CH—C=O (59 ppm), —CH$_2$—N—CH$_2$— (65.5 ppm), —CH$_2$—O—CH$_2$— (68 ppm), and C=O (178 ppm).

P(AcMo-co-APSA) copolymerization reaction was carried out by an equimolar feed ratio of both monomers. To this, 0.030 mol of AcMo (6.210 g) and 0.030 mol of APSA (4.230 g) were added to the copolymerization flask. The initiator AP (1 mol %; 0.0004 mol. 0.137 g) was added, and the reaction was kept at 60°C for 24 h. After this, the polymer was lyophilized.

Yield: 98%. FT-IR spectrum (KBr pellets) shows the following characteristic absorption bands: C—C (2931 cm$^{-1}$), O—CH$_2$ (2859 cm$^{-1}$), C=O (1629 cm$^{-1}$), O—C—O (1110 cm$^{-1}$), C—S (620 cm$^{-1}$), and S=O (1167 cm$^{-1}$). $^1$H NMR spectrum (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the following signals: —CH$_3$ and —CH$_2$— (between 1.40 and 1.52 ppm), —CH— (3.1 ppm), NH—CH$_2$—, —CH$_2$—N—CH$_2$—, and —CH$_2$—O—CH$_2$— (between 3.4 and 3.7 ppm). $^{13}$C NMR spectrum (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the following carbon signals: —CH$_3$ (27 ppm), —CH$_2$—CH— (38 ppm), —N—CH$_2$— (44 ppm), —CH$_2$—SO$_3$H (48 ppm), CH—C=O (59 ppm), —CH$_2$—N—CH$_2$— (65.5 ppm), —CH$_2$—O—CH$_2$— (68 ppm), and C=O (178 ppm).

All the copolymers were purified through the ultrafiltration membrane, with a molar mass cut off of 3000 Da.

To compare the metal ion retention properties, the other two homopolymers, P(AAm) and P(APSA), were also synthesized by radical polymerization. For the polymerization of AAm, 2,2′-azoisobutyronitrile, AIBN was used as initiator. The reaction was kept at 60°C for 10 h. Yield: 99%. For the polymerization of APSA, AP was used as initiator. The reaction was kept at 70°C for 24 h. Yield: 99%.

### Poly(acrylamide)

The FT-IR spectrum (KBr pellets) shows among the most important absorption signals at N—H (3401 cm$^{-1}$) and C=O (1677 cm$^{-1}$). $^1$H NMR (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the signals corresponding to methylene and methyne protons, at 1.62 ppm and 2.14 ppm, respectively.

### Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)

The FT-IR spectrum (KBr pellets) shows the most important absorption bands: C=O, amide (1647 cm$^{-1}$), C—H (2930 cm$^{-1}$), C—N, amide (between 1400 and 1450 cm$^{-1}$). $^1$H NMR spectrum (250 MHz, D$_2$O, 25°C, TMS as internal standard) shows the following signals: between 3.1 and 3.5 ppm (CH$_2$—SO$_3$H) and CH$_3$ (1.35 ppm).
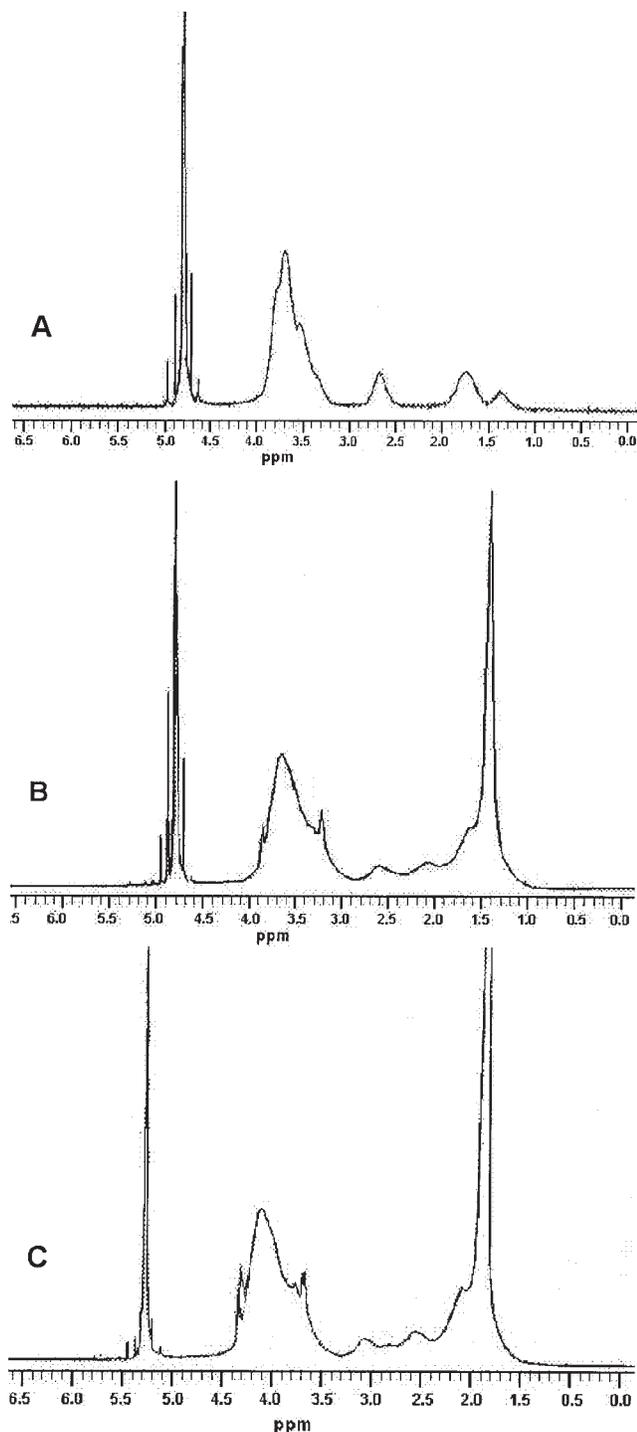
**Figure 1** ¹H NMR (250 MHz, D₂O) spectra of (A) P(AcMo), (B) P(AcMo-*co*-AAm), and (C) P(AcMo-*co*-APSA).

## Metal ion binding capacity procedure

For the determination of the complexing binding ability, an aqueous solution of polymer (0.20 m$M$) was prepared and adjusted to the corresponding pH, by addition of dilute $HNO_3$ or NaOH. The solution of polychelatogen and metal nitrate (0.08 m$M$) was placed in a 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 10,000 g mol$^{-1}$ was used. The filtration fractions ($Z = 1$–10) were collected, and the concentrations of metal ions in the filtrate were 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 ($V_0$).

## Measurements

The FT-IR spectra were recorded on a Magna Nicolet 550 spectrophotometer. The ¹H NMR spectra were recorded in $D_2O$, using a Bruker Multinuclear AM 250 spectrophotometer (Fig. 1).

The pH was determined with a Jenco Electronics 1671 pH-meter. For the LPR technique, a membrane filtration system was employed, to test the coordinating properties of the polychelatogen. A Unican Solaar M5 Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

## RESULTS AND DISCUSSION

WSPs containing amine, amide, and sulfonic acid groups were synthesized by radical polymerization. Thus, new polymers, such as P(AcMo), P(AcMo-*co*-AAm), and P(AcMo-*co*-APSA), were synthesized. P(AAm) and P(APSA) were also synthesized, to be able to compare the metal ion retention properties, under the same synthetic procedures (Scheme 1).
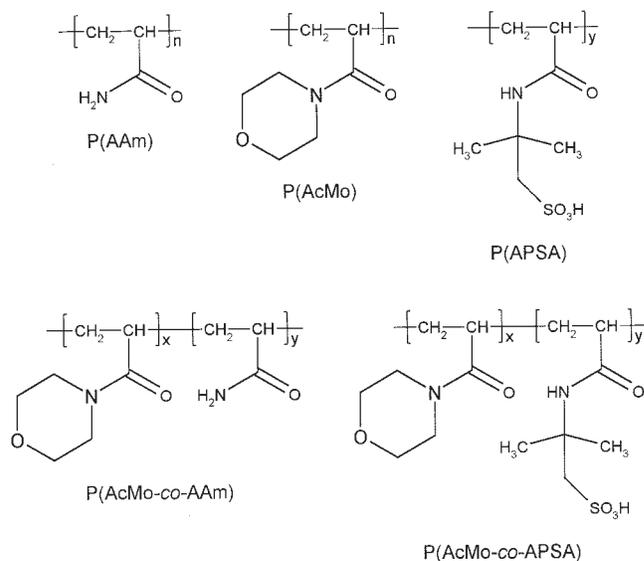


**Scheme 1**
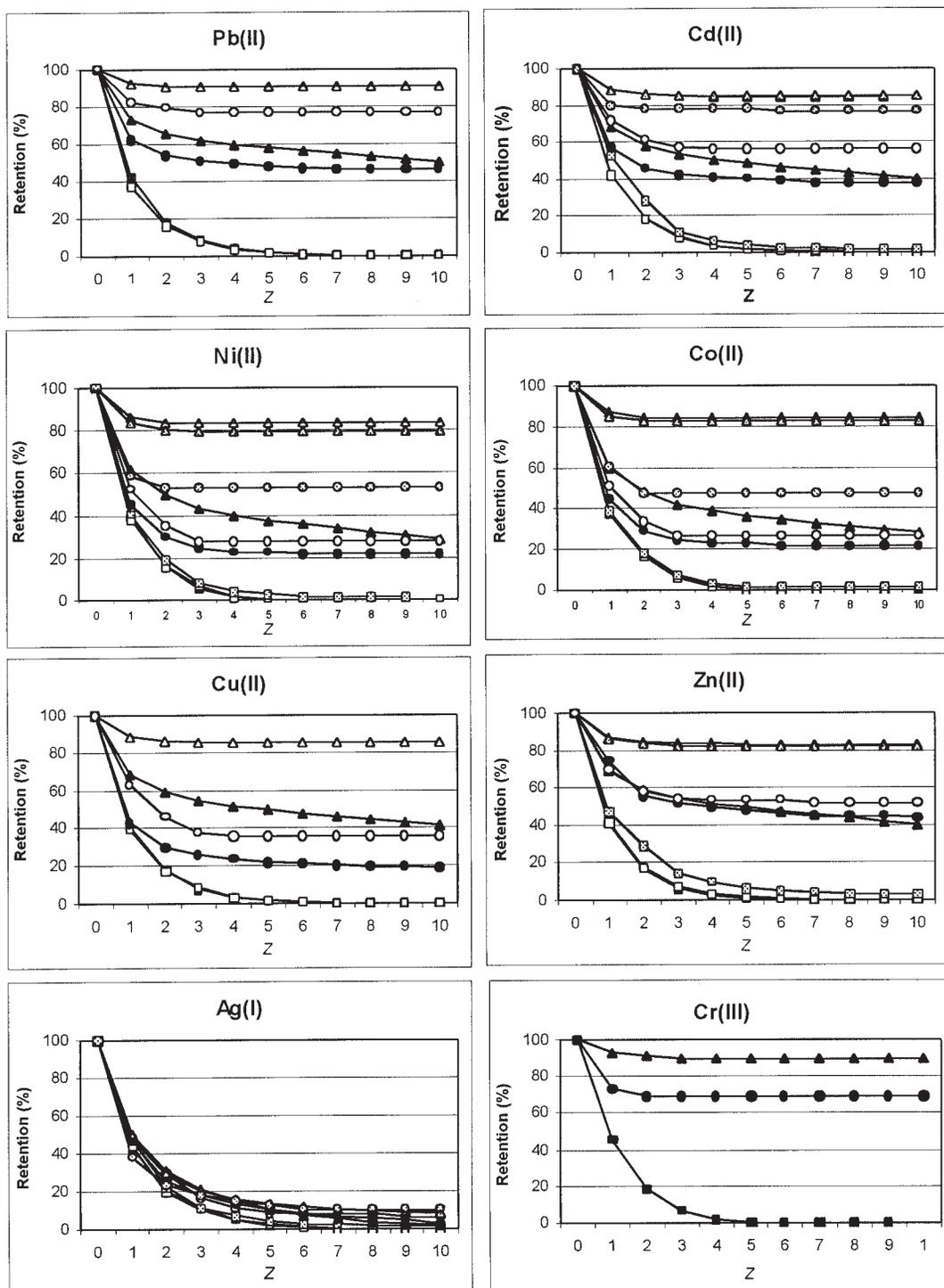
**Figure 2** Retention profiles of the polychelatogens at different pH. P(AcMo) ■, P(AcMo-*co*-AAm) ▲, P(AcMo-*co*-APSA) ●
bold, pH 3, white, pH 5, and gray pH 7.

The polymers were characterized by spectroscopy and its structures were confirmed. All the data are included in the experimental part.

Owing to the high copolymerization yield (>95%), the monomer reactivity ratios were not determined.

The metal ion retention ability of the WSPs was studied by the LPR technique, using the washing method. The metal ion retention profiles were also determined (see Figs. 2 and 3). It was found that P(AcMo) does not form stable complexes through the tertiary amino groups, with all the metal ions studied [see Fig. 3(a)]. A similar retention behavior was shown by P(AAm). P(APSA), a strong polyelectrolyte, shows a high retention at all pH, for di- and trivalent cations.
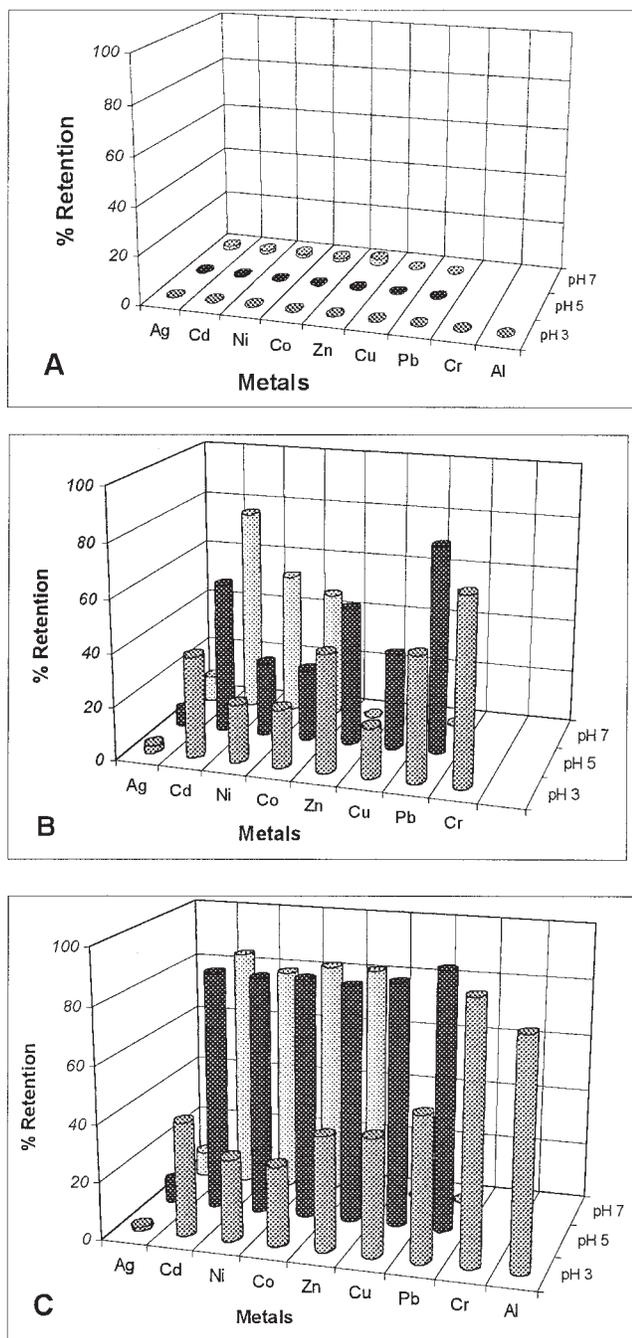
**Figure 3** Metal ion retention of polychelatogens, at different pH and $Z = 10$.

At pH 1, only $Cr^{3+}$ shows a retention higher than 30% at $Z = 10$. At pH 3, the retention is higher, 90% for $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Zn^{2+}$ and 100% for $Cr^{3+}$. At pH 5 and 7, the metal ion retention is close to 100%. Only $Ag^+$ shows a weak interaction (30% at $Z = 10$). This is because $Ag^+$, a monovalent ion, shows an electrostatic interaction with the sulfonate groups, which is different with respect to the di- and trivalent cations.

The copolymer P(AcMo-*co*-AAm) shows a synergic effect. Thus, at pH 3, a high efficiency and selectivity

for trivalent cations $Cr^{3+}$ and $Al^{3+}$ were observed. The highest retention was achieved at pH 5 for the divalent cations $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$, with retention values close to 85% [see Fig. 3(c)].

By combining tertiary amino and sulfonic acid groups at the P(AcMo-*co*-APSA), the retention was for $Cr^{3+}$ (60% at pH 3), $Pb^{2+}$ (75% at pH 5), and $Cd^{2+}$ (77% at pH 7) [see Fig. 3(b)]. In this case, the metal ion retention is higher than that for P(AcMo), but lower than that of P(AcMo-*co*-AAm). This is because AcMo moiety is not only a poor ligand, but also hinders the interaction of the metal ions with the sulfonate groups.

The filtration factor $Z$ is a parameter for the measurement of the polymer ligand–metal ion interaction strength. Figure 3 shows the retention behavior of the polychelatogens at different pH and $Z = 10$. Thus, P(AcMo-*co*-AAm) forms more stable complexes than P(AcMo-*co*-APSA). At pH 3, the trivalent cations, $Cr^{3+}$ and $Al^{3+}$ form the most stable complexes with both copolymers. Cr(III) is less toxic, less soluble, and less mobile than Cr(VI). The interaction of $Ag^+$ with both copolymers is very weak.

### Polymer–metal ion interaction mechanism

The interaction is strongly related to the dissociation degree of the polychelatogens. Thus, for P(AcMo), most of the ligand groups are existing as free amines at pH 5. P(APSA) is deprotonated at a lower pH value than that of a carboxylic acid. Because of this, P(APSA) shows a high metal ion retention capability. For this polychelatogen, the polymer–metal ion interaction can be assumed to be predominantly of the electrostatic type.

### CONCLUSIONS

Novel WSPs, such as P(AcMo), P(AcMo-*co*-APSA), and P(APSA) were synthesized by radical polymerization. These WSPs containing tertiary amino, amide, and sulfonic acid groups were investigated as polychelatogens, by using the LPR technique. P(AcMo) did not retain any metal ions, probably due to the steric hindrance of the tertiary amino group. In contrast, P(AcMo-*co*-APSA) showed the highest metal ion retention capability, according to a synergic effect and exhibited the most metal ion–polymer interactions, at all pH. It showed a metal ion retention capability higher than that of P(AcMo), but lower than that of P(APSA). Consequently, the sulfonate groups were the most active ligand groups in the copolymers.

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