

Removal of Metal Ions by Water-Soluble Polymacromonomers in Conjunction with Ultrafiltration Membrane

Bernabé L. Rivas, S. Amalia Pooley, Antonio Maureira

Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

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ABSTRACT: The macromonomer polyethylene glycol methylether methacrylate was homo- and copolymerized with 2-acrylamido-2-methyl-1-propane sulfonic acid under three feed monomer ratios. The initiator used was ammonium peroxydisulfate (0.2 mol %). All the polymers were completely soluble in water. The copolymer composition was determined by elemental analysis. The metal ion interaction capability of the three polymers was investigated through the liquid-phase polymer-based retention (LPR) technique at different values of pH and filtration factor Z . The highest metal ion retention ability was observed at pH

5.0. The homopolymer showed a high selectivity for Ni(II) ions at pH 3.0. The copolymers (PEGMEM)_{1.51-co}-(APSA)_{1.00} and (PEGMEM)_{1.00-co}-(APSA)_{1.95} showed a high selectivity for Cr(III) ions at pH 3.0. The maximum retention capacity, in general, was similar for the homo- and copolymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2955–2960, 2004

Keywords: water-soluble polymers; membranes; metal ions; macromonomers; liquid-phase polymer-based retention (LPR)

INTRODUCTION

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.^{1–20} The possibility of synthesizing derivatives of commercially available WSPs, to achieve selective metal ion complexation, was recognized early on. Thus, a number of soluble and hydrophilic polymers have been prepared through addition polymerization and by functionalizing various polymers, and were found to be suitable for the separation and enrichment of metal ions in conjunction with membrane filtration. Membrane filtration easily allows the separation of metal ions bound to soluble polymers from nonbound metal ions. This method is known as the liquid-phase polymer-based retention (LPR) technique.^{1,3}

A wide range of applications have been investigated, including the nuclear industry and the removal of toxic heavy metal ions such as Pb(II), Cd(II), and Hg(II).^{21–25} WSPs are commercially available or can be synthesized by different routes. Among the most important requirements for technological applications of

these polymers are the high solubility in water, an easy and cheap route of synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest. The main features of an LPR system are a filtration cell with a magnetic stirrer containing a membrane filter with a known exclusion rating, a reservoir, and a pressure source (e.g., a nitrogen bottle). Different modes of separation by LPR can be used for inorganic ions.^{1–11} The washing method is a batchlike method, in which a liquid sample containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at given pH and ionic strength values. This is then washed with a water solution that may reproduce the same pH and ionic strength values. Conditions may be found where the ions of interest are retained and other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolute. In the enrichment method, analogous to an in-column method, a solution containing the metal ions to be separated is passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both cell and reservoir solutions may be adjusted to the same values of pH and ionic strength.

During the last decade, special attention has been paid to the well-controlled synthesis and thorough characterization of macromonomers and to their ability to undergo homo- and copolymerization with vinyl comonomers.^{26–28} Actually, a large variety of macromonomers

Correspondence to: B. Rivas (brivas@udec.cl).

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serve as precursors of graft copolymers of great potential such as coatings adhesives, compatibilizers, emulsifiers, and biomaterials, for example.^{29,30}

Therefore, the aim of this study was to investigate the metal ion retention capability through the LPR technique of a new macromolecular architecture like that of polymacromonomers.

EXPERIMENTAL

Reagents

The macromonomer polyethylene glycol methylether methacrylate (PEGMEM), (Aldrich, Milwaukee, WI) was homo- and copolymerized with 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA; Aldrich) under three feed monomer ratios. Ammonium peroxydisulfate (AP) was used as initiator (0.2 mol %).

The metal salts were commercially available (Merck, Stuttgart, Germany) and of analytical reagent grade.

Synthesis of the water-soluble chelating polymers

Three copolymers of PEGMEM and APSA were synthesized by radical-solution (water) polymerization using AP as initiator (0.2 mol %) and varying the feed monomer ratio but keeping the total amount constant (0.02 mol). The polymers were purified and fractionated by ultrafiltration with a membrane with a molar mass cutoff (MMCO) of 100,000 g mol⁻¹. The polychelators were lyophilized and characterized by FTIR and NMR spectroscopy.

Ultrafiltration of the metal ions

To determine 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 polychelator and metal nitrate (0.08 mM) was 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 10,000 g mol⁻¹ was used. The filtration fraction ($Z = 1-10$) was collected 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_o).

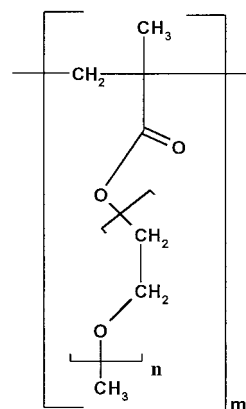
Characterization

FTIR and NMR spectra were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI) and Bruker AC 250 multinucleus spectrometer (Bruker Instruments, Billerica, MA), respectively. The thermal properties were

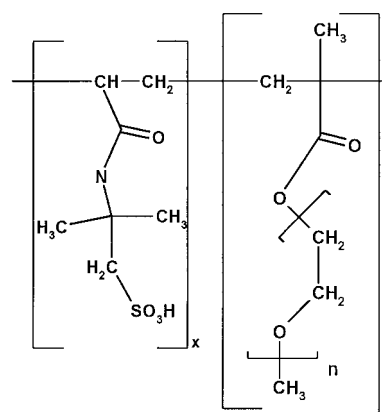
studied under nitrogen atmosphere by an STA 625 thermal analyzer (Polymer Laboratories, Amherst, MA). The metal ions in the filtrate were determined with a Unicam Solaar M Series flame and furnace atomic absorption spectrometer system (UK).

RESULTS AND DISCUSSION

Water-soluble polymers containing ligand groups were obtained by radical homo- and copolymerization reaction of the macromonomer polyethylene glycol methylether methacrylate. The comonomer was the strong polyelectrolyte 2-acrylamido-2-methyl-1-propane sulfonic acid. The copolymerization reactions were conducted under three feed monomer ratios by using 0.2 mol % AP as initiator at 60°C by 48 h. The structures of the polymacromonomer and copolymers are shown below.



(PEGMEM)



PEGMEM-co-APSA

The reactivity of the APSA counit is higher than that of the PEGMEM counit because copolymers 2 and 3 are the richest in APSA units (see Table I).

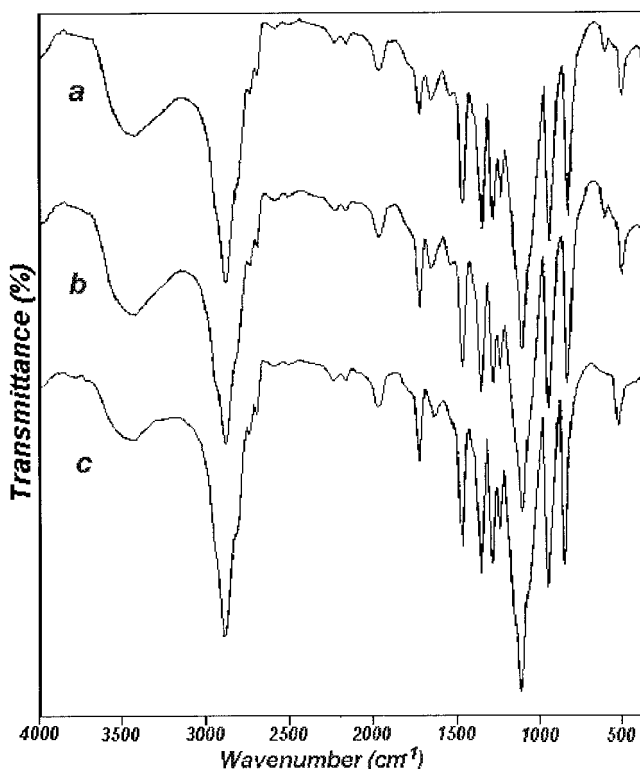


Figure 1 FTIR spectra of the PEGMEM-co-APSA copolymers: (a) PEGMEM_{1.00}-co-APSA_{4.16}; (b) PEGMEM_{1.00}-co-APSA_{1.95}; and (c) PEGMEM_{1.51}-co-APSA_{1.00}.

Before investigation of the metal ion retention capability, all the polymers were passed through ultrafiltration membranes with MMCO values of 50,000 and 100,000 Da. Fractions over 100,000 Da were used for subsequent experiments. Figure 1 shows the FTIR spectra of the polymacromonomers.

The binding and elution processes may be formulated as a chemical reaction, in which a reversible interaction reaction of the metal ion with the polymer, in combination with an irreversible transfer of metal ions across the membrane, is responsible for the metal ion retention. The influence of the membrane in the retention of metal ions inside the ultrafiltration cell is low and may be considered negligible in most cases. This cannot be said in the case of organic low molecular weight molecules.

There is a strong dependency of the metal ion retention capability with the pH. The PEGMEM at pH 3 and $Z = 10$ shows a low metal ion retention capacity but a very high selectivity for Ni(II) ions. Ni(II) would form a stable complex with coordination number 4, which is very difficult to oxidize. According to the literature³¹ the interaction of the Ni(II) would occur through the donor oxygen atom from the ethylene glycol group. At pH 5 it increases the retention of all metal ions, except Cr(III), which precipitates at such pH. At pH 7, it strongly diminishes the retention of all the metal ions, which could be attributed to hydrogen bridge interactions between the polymer side chains that did not facilitate the polymer-metal ion interaction.

Incorporation of the sulfonic acid as a ligand group to the polymer chain increases the metal ion retention at pH 3, particularly for Ag(I) and Cr(III) ions (see Table II, copolymers 1 and 2). The copolymer with the highest content of APSA unit shows a very poor retention capability. Only Ag(I) at pH values of 3 and 7 and Cu(II) ions at pH 5 are retained. It was lower than 40 and 20% for Ag(I) and Cu(II), respectively. The most important feature is the high selectivity for Cr(III) ions at pH 3. These ions are retained over 75% (1.16 meq/g of dry polymer). This is basically attributed to the active participation of the APSA unit because the PEGMEM did not retain this ion. This can be attributed to the Pearson's principle.³² Cr(III) ion is a hard acid and the sulfonic acid also favors the ligand-metal ion interaction. For the same reason, soft acids like Ag(I), Cd(II), and Pb(II) would interact more actively with the PEGMEM unit than that of the APSA unit. Cu(II), Co(II), and Ni(II) are borderline, and thus their retention is lower than 50%. The monovalent silver cations show a weak electrostatic interaction with the ligand groups (see Figure 2).

Determination of maximum retention capacity (mrc)

MRC was determined by the enrichment method according to the LPR technique. The method consists in passing other metal ion solutions, with a known concentration, through a solution of water-soluble polymer (20 mL). The volume of the water-soluble poly-

TABLE I
Feed Monomer Ratio and Copolymer Composition

Acronym	Feed monomer ratio PEGMEM : APSA	Copolymer composition ^a PEGMEM : APSA	Yield (%)
PEGMEM-co-APSA 1	3.0 : 1.0	1.51 : 1.00	92
PEGMEM-co-APSA 2	1.0 : 1.0	1.00 : 1.95	95
PEGMEM-co-APSA 3	1.0 : 3.0	1.00 : 4.16	91

^a Determined by elemental analysis.

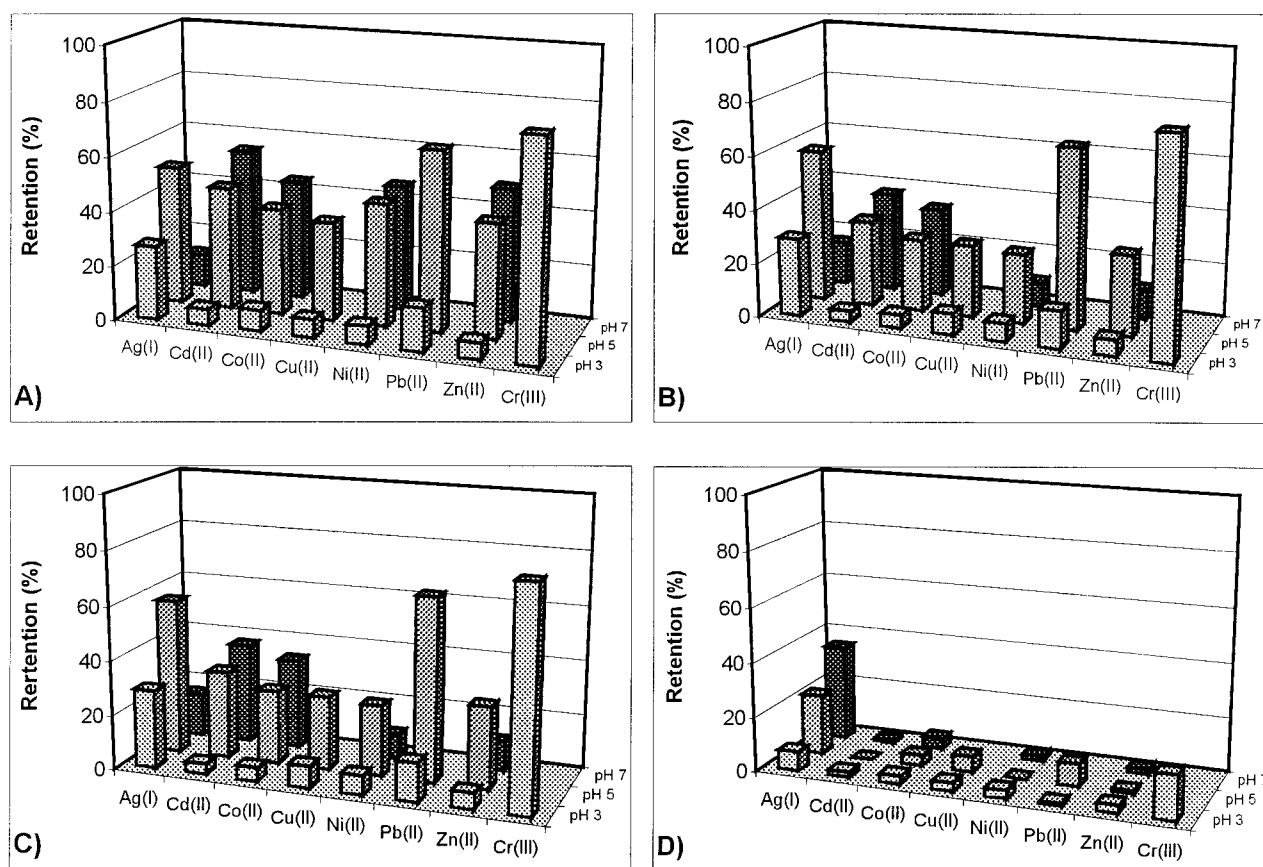


Figure 2 Metal ion retention (Retention %) of the polymers: (A) PEGMEM; (B) PEGMEM-*co*-APSA 1; (C) PEGMEM-*co*-APSA 2, (D) PEGMEM-*co*-APSA 3; at different pH values. Polymer : metal ion ratio (in mol) 40 : 1. Temperature: 20°C; cell volume: 20 mL.

mer was kept constant and the metal ion content was determined in the different filtrate volumes.

In the enrichment method, a polymer solution is placed inside the ultrafiltration cell, and a metal-ion solution is placed in the reservoir. When the reservoir solution is passed through the polymer solution, the macromolecules uptake metal ions until saturation is achieved. With this procedure, maximum capacities of the polymer can be calculated, defined as the maximum amount of metal ions bound to the polymer per unit polymer. Plotting the concentration of the metal species in the filtrate versus Z helps to make this calculation. A control experiment, in the absence of the

polymer, is needed. The concentration in the filtrate increases until it achieves the concentration of the reservoir solution because it is controlled by diffusion. When the water-soluble polymer is present in the cell solution, if an irreversible uptake of metal ions is carried out, a parallel curve to the plot of the blank experiment will appear at a higher Z value.

Because the metal ion interactions are processes in equilibrium, a lower slope in the rate of increase of the metal concentration in the filtrate is normally observed. From the differences in the slopes, the amounts of metal ions bound to the polymer and free in the solution can be easily calculated.

TABLE II
Experimental Conditions to Determine the CMR of the Polymers

Acronym	Polymer (g)	Metal ion concentration (ppm)						
		Ag(I)	Cd(II)	Co(II)	Ni(II)	Pb(II)	Zn(II)	Cr(III)
PEGMEM	0.461	635	451	235	235	831	261	210
PEGMEM- <i>co</i> -APSA 1	0.266	635	451	235	235	831	261	210
PEGMEM- <i>co</i> -APSA 2	0.179	635	451	—	—	831	—	210
PEGMEM- <i>co</i> -APSA 3	0.233	—	—	—	—	831	—	—

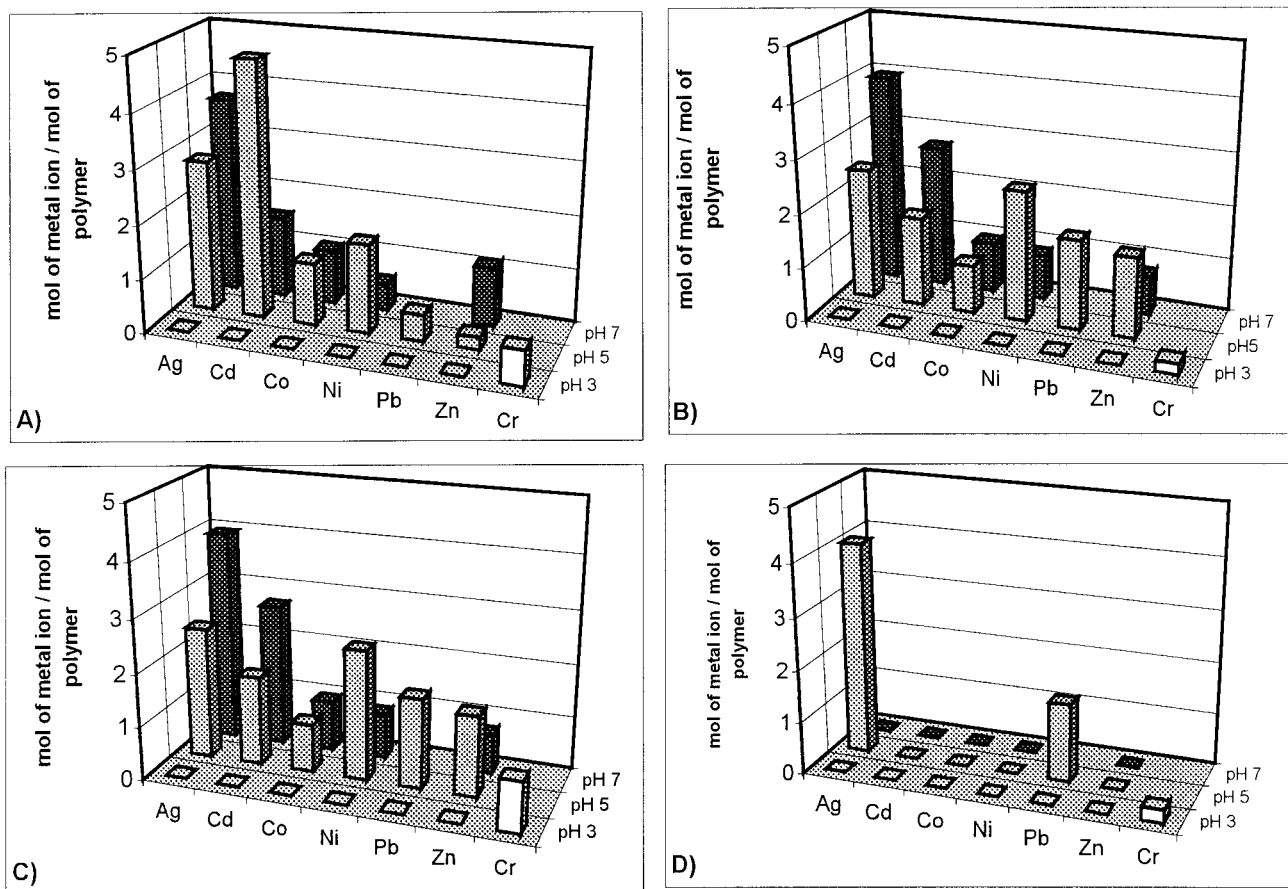


Figure 3 Maximum retention capacity (MRC) of the polymers for the metal ions at different pH values: (A) PEGMEM; (B) PEGMEM-co-APSA 1; (C) PEGMEM-co-APSA 2; (D) PEGMEM-co-APSA 3.

The general experimental conditions for determination of the MRC values are summarized in Table II.

The MRC was determined for the metal ions with a retention capacity higher than 40% at $Z = 10$. The fractions used have a molecular weight over 50,000 Da. By comparing the curves of the metal ion concentration in the filtrate versus filtrate volume with the corresponding blank run, it is possible to obtain the necessary filtrate volume to achieve the MRC for each metal ion.

With this volume and by the relationship

$$\text{MRC} = (MV)/P_m$$

where MRC is expressed as milligrams of metal ion retained per gram of polymer; M is the metal ion concentration of metal ion (mg/L); V is the filtrate volume through the membrane free of metal ion (L); and P_m is the mass of polymer (g), it is possible to calculate the MRC values.

The results are shown in Figure 3. The highest MRC values correspond to Ag(I) at pH values of 5 and 7, 2.8 and 3.7 mol of metal ion/mol of repeat unit, respectively; Cd(II) at pH values of 5 and 7, 4.8 mol of metal

ion/mol of repeat unit. These high MRC values are attributed to the interaction with the ethylene glycol and sulfonic groups (see Figure 4).

The MRC values of the copolymers did not increase significantly with respect to the homopolymer P(PEGMEM), except for Pb(II) at pH 5, particularly for the PEGMEM-co-APSA 1:1.95, which has an excess of APSA count.

The results for the metal ions at different pH values and concentrations are summarized in Table II. There is a clear difference between the MRC values for the mono, divalent, and trivalent metal ions. It is lower for Cr(III) and the MRC values for the divalent cations are very similar, which would demonstrate that the polymer-metal ion interaction is the electrostatic type with the APSA count. This would explain why the MRC for a trivalent cation like Cr(III) is lower than that of a divalent cation like Cu(II), Co(II), and Ni(II). This is theoretically attributable to one Cr(III) ion interacting with three negative charges coming from APSA repeat counts, whereas a divalent cation such as Co(II) will do it only with two. Hence, to neutralize completely the charges in the APSA count, partially or com-

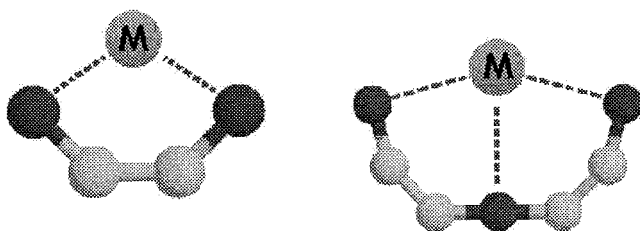


Figure 4 Possible metal ion interaction between the ethylene glycol moiety and metal ions. M, metal ion.

pletely dissociated, a higher number of divalent ions than trivalent cations will be necessary, and consequently the MRC will be higher for the former.

On the other hand, the metal ion retention behavior of P(APSA) can be treated according to the condensation theory.^{33,34} In this sense, it is suggested that there is a number of condensated counterions to the polyelectrolyte in a determined volume. These condensated ions are in equilibrium with a determined number of gegenions out of the condensation volume. Amounts of free and condensated ions basically depend on the lineal charge density parameter ξ . It assumes that the theoretical value for the metal ion retention with a polyelectrolyte will never be achieved.

CONCLUSIONS

The water-soluble polymacromonomers from PEG-MEM and APSA comonomers were synthesized by radical polymerization. Their metal ion retention capability was investigated through the LPR technique. There was a strong dependency of the metal ion retention capability on the pH. The PEGMEM at pH 3 and $Z = 10$ shows a low metal ion retention capacity but a very high selectivity for Ni(II) ions. The incorporation of sulfonic acid as a ligand group to the polymer chain increases the metal ion retention at pH 3, particularly for Ag(I) and Cr(III) ions. The copolymer with the highest content of APSA unit shows a very poor retention capability. Only Ag(I) at pH values of 3 and 7 and Cu(II) ions at pH 5 were retained. It was lower than 40 and 20% for Ag(I) and Cu(II), respectively. The most important feature is the high selectivity for Cr(III) ions at pH 3.

The MRC values of the copolymers did not increase significantly with respect to the homopolymer P(PEGMEM), except for Pb(II) at pH 5, particularly for the PEGMEM-co-APSA 1 : 1.95, which has an excess of APSA counts.

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