Synthesis of Copolymers Containing Opposite Charged Comonomers and Their Interactions with Metal Ions

Bernabé L. Rivas,[1] Eduardo D. Pereira[2]

[1]Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile
[2]Analytical and Inorganic Chemistry Department, University of Concepción, Casilla 160-C, Concepción, Chile

ABSTRACT: Radical polymerization was used to synthesize three copolymers of [3-(methacryloylamino)propyl]trimethylammonium chloride and methacrylic acid [P(MPTA-co-MA)]; three copolymers of MPTA and 2-acrylamido-2-methyl-1-propane sulfonic acid [P(MPTA-co-APSA)], which had different feed monomer mole ratios but a constant total number of moles (0.03 mol); and the homopolymers poly(MPTA), poly(MA), and poly(APSA). The yields for all homopolymers and copolymers were over 70 and 90%, respectively. All products were dissolved in water, purified, and fractioned by an ultrafiltration membrane with different exclusion limits of the molecular weight (3,000, 10,000, 30,000, and 100,000 g mol^{-1}). All fractions were lyophilized. The polymeric materials were characterized by FTIR and ^{1}H-NMR spectroscopy. The metal ion interaction with the hydrophilic polymers was determined as a function of the pH and the filtration factor. It was dependent on the pH, type of ligand group, and charge of the metal ion. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1715–1721, 2003

Key words: water-soluble polymers; ultrafiltration membranes; metal ions

INTRODUCTION

The continuous increase of world needs for most of the known metals and strict environmental regulations make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at low concentrations. Polymeric insoluble supports have been widely investigated and applied for metal recovery from dilute solution.[1–5] These two heterogeneous phases can be avoided by the application of separation methods based on membrane processes, which are among the most promising techniques for enrichment of various species from solutions.[6,7] Thus, a number of soluble and hydrophilic polymers have been prepared through polymerization and by functionalizing various polymers, and they have been found to be suitable for the separation and enrichment of metal ions in conjunction with membrane filtration. Membrane filtration allows the easy separation of metal ions bound to soluble polymers from nonbound metals. This method is known as *liquid-phase polymer based retention* (LPR).[8] Applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration is the most suitable technique for LPR studies, and a vast amount of data have been published.[9–22]

This article reports the synthesis of copolymers containing ammonium and carboxylic groups and describes their characterization by spectroscopy. These copolymers and those containing ammonium and sulfonic acid groups are investigated by the LPR technique at different pH values and filtration factors (Z) as polychelatogens to determine the metal ion retention capability. The metal ions studied are Ag$^+$, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Cr^{3+}.

EXPERIMENTAL

Reagents

The methacrylic acid (MA, Aldrich) used in the study was previously distilled. [3-(Methacryloylamino)propyl]trimethylammonium chloride (MPTA, Aldrich), 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA, Aldrich), ammonium persulfate (APS, Aldrich), and analytical grade metal salts (Merck) were used as received.

Synthesis of homopolymers

Poly(MPTA) (PMPTA), poly(MA) (PMA), and poly-(APSA) (PAPSA) were synthesized by radical polymerization as previously described.[23] The yield for all homopolymers is over 70%. PMPTA: (C$_{10}$H$_{21}$ONCl)$_n$

$(206.5)_n$ FTIR (KBr): 2958 (s, C—H), 1638 (s, C=O amide), 1365 cm^{-1} (C—N quaternary amine). ^{1}H-NMR (D$_2$O, TMS, room temperature): δ 3.85 (N—CH$_2$—CH$_2$), 3.50 (CH$_2$—CH$_2$—CH$_2$), 3.30 [N—(CH$_3$)$_3$], 2.15 (C—CH$_2$ and CH$_2$—CH$_2$—CH$_2$), 1.10 ppm (C—CH$_3$). PMA: (C$_4$H$_6$O$_2$)$_n$ (86)$_n$ FTIR (KBr): 3439 (s, O—H), 2930 (s, C—H), 1710 cm^{-1} (s, C=O carboxylic acid). ^{1}H-NMR (D$_2$O, TMS, room temperature): δ 2.15 (C—CH$_2$), 1.1–1.4 ppm (C—CH$_3$). PAPSA: (C$_7$H$_{13}$O$_4$NS)$_n$ (207)$_n$ FTIR (KBr): 2930 (s, C—H), 1647 (s, C=O amide), 1400–1450 cm^{-1} (C—N amine). ^{1}H-NMR (D$_2$O, TMS, room temperature): δ 3.2–3.5 (C—CH$_2$—SO$_3$H), 1.95 (H—C—CH$_2$), 1.45 ppm [C—(CH$_3$)$_2$].

Synthesis of P(MPTA-*co*-APSA)

Three copolymers with different feed monomer mole ratios were synthesized by radical polymerization as previously described.[23] The structures of P(MPTA-*co*-APSA) and P(MPTA-*co*-MA) are as follows:
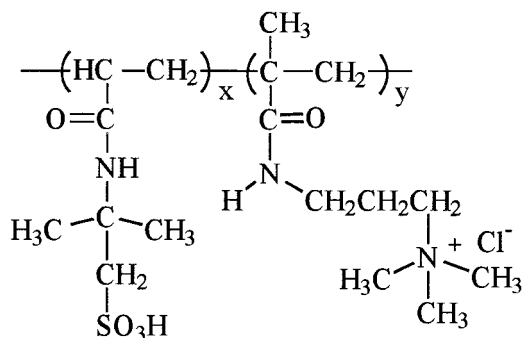
P(MPTA-*co*-APSA)
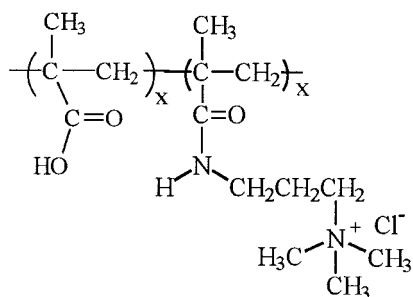
P(MPTA-*co*-MA)

Scheme 1

Synthesis of P(MPTA-*co*-MA)

Three copolymers with different feed monomer mole ratios but a constant total number of moles (0.03 mol) were synthesized. APS (1 mol %) was used as an initiator. The polymer reaction was kept under N$_2$ at 70°C for 24 h. The copolymers were purified by an ultrafiltration membrane. The yield was higher than 90%.

All products were dissolved in water, purified, and fractioned by an ultrafiltration membrane with different exclusion limits for the molecular weight (3,000, 10,000, 30,000, and 100,000 g mol^{-1}). All fractions were lyophilized.

Characterization

The FTIR spectra were recorded on a Magna Nicolet 550 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC 250 P Multinucleous spectrometer.

For the light scattering measurements, the concentration series was prepared in cylindrical sample cells by directly filtering aliquots of the stock solution and solvent using nylon membrane filters with a 0.45 μm pore size for the polymer solution and 0.2 μm for the the solvent. This clarification method gave consistent results for the scattered light, and no anomalous angular dependence in the dialyzed samples and good constancy in repeated scans of the same sample. The intensity of light scattered by the solutions was recorded with a Dawn DSP-F multiangle laser light scattering photometer (Wyatt Technology Co.) equipped with an argon-ion laser ($\lambda_0 = 488$ nm) as a source. The primary beam is vertically polarized, and there is a set of 18 detectors that are equally spaced in cotangent θ (where θ is the angle measured with respect to the direction of the laser beam). The system allows the recording of the light intensity at 15 selected angles. All measurements were done at 25°C in batch mode using cylindrical sample cells.

The differential refractive index increment (*dn/dc*) was determined with an interferometric refractometer (Optilab 903, Wyatt) calibrated with aqueous NaCl and operating at the same wavelength as the laser photometer. The sample solutions were 0.5–4.0 mg/mL. In this range, all samples showed good linear variation of the refractometer reading with the sample concentration and the *dn/dc* value was calculated by linear regression analysis.

The thermal stability of the polymers and copolymers was studied under N$_2$ using a thermoanalyzer (STA 625, Polymer Laboratories). A UNICAM SOLAAR M series atomic absorption spectrometer was used for the determination of the metal ion concentration filtrate.

Procedure to study metal ion retention ability

The aqueous solutions of polymer and copolymers (0.2 m*M*) and metal nitrates (0.05 m*M*) were placed into the filtration cell. The total volume of 20.0 mL was

TABLE I
Experimental Conditions and Results of Copolymerization of MPTA with APSA and MA

Sample	Monomeric Mole Ratio in Feed MPTA/APSA	MPTA Mmol	Volume (mL)	APSA Mmol	Mass (mg)	Copolymer Composition MPTA/APSA	Yield (%)
P(MPTA-co-APSA)11	1.0:1.0	14.5	6.4	14.5	2.99	NS[b]	NS[b]
P(MPTA-co-APSA)21	2.0:1.0	19.4	8.6	9.60	2.00	1.4:1.0	94
P(MPTA-co-APSA)12	1.0:2.0	9.60	4.2	19.4	4.00	1.0:3.47	98

	MPTA/MA	MPTA Mmol	Volume (mL)	MA Mmol	Mass (mg)	MPTA/MA	
P(MPTA-co-MA)11	1.0:1.0	14.5	6.4	14.5	1.23	NS[b]	NS[b]
P(MPTA-co-MA)21	2.0:1.0	19.4	8.6	9.60	0.82	1.3:1.0	91
P(MPTA-co-MA)12	1.0:2.0	9.60	4.2	19.4	1.65	1.0:2.7	95

[a] Determined by ^{1}H-NMR spectra.
[b] It is insoluble in water.

TABLE II
Macromolecular Dimensions and Weight-Average Molecular Weight (M_w) of Products, as Determined by Light Scattering

Sample	Fraction Used (D)	Solvent	dn/dc (mL/g)	$<S^2>^{1/2}$ (nm)	$M_w \times 10^{-3}$ (g/mol)	$A_2 \times 10^4$ (mol mL/g^2)
P(MPTA-co-APSA)21	30,000–100,000	0.5M HCl	0.1475	27.7	1.2	2.06
P(MPTA-co-APSA)21	>100,000	0.5M HCl	0.1464	28.4	4.53	1.53
P(MPTA-co-APSA)21	>100,000	0.5M HCl dialyzed	0.1467	28.9	4.37	1.66
P(MPTA-co-APSA)12	30,000–100,000	0.5M HCl	0.1520	26.2	0.56	3.31
P(MPTA-co-APSA)12	>100,000	0.5M HCl	0.1540	32.8	3.85	1.82
P(MPTA-co-APSA)12	>100,000	0.5M HCl dialyzed	0.1540	35.0	3.97	2.07
P(MPTA-co-MA)21	>100,000	0.5M HCl	0.1450	74.0	9.19	4.13
P(MPTA-co-MA)12	>100,000	0.5M HCl	0.1480	65.6	7.23	3.56

The refractive index increment is determined by differential refractometry.

kept constant. The reservoir contained water adjusted to the same pH as the cell solution. The filtration runs were carried out over a membrane with an exclusion rating of 5000 D. The system was pressurized (300 kPa) and kept at room temperature. Then the cell solution was stirred and washed with the reservoir fluid. Filtration fractions were collected and the metal concentrations analyzed by atomic absorption spectroscopy. The metal ions that were studied were Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Cr^{3+}; Hg^{2+} was not studied at a pH over 2 and chromium at a pH over 3 to avoid precipitation.

RESULTS AND DISCUSSION

Polyelectrolytes containing cationic, anionic, and cationic and anionic groups were obtained by radical polymerization.

Copolymers containing either ammonium or sulfonic groups were synthesized (Table I). The copolymer composition was determined through the ^{1}H-NMR spectra by a comparison of the integration area of the characteristic proton signal of each monomer (Fig. 1). Thus, the signal at 3.2 ppm corresponding to nine protons of the methyl groups coming from the MPTA monomer unit was compared to that at 1.6 ppm attributed to six protons of the methyl groups belonging to the APSA monomer unit. According to the data, the incorporation of the APSA comonomer is favored. It may be explained as being due to their lower steric hindrance and higher reactivity than that of MPTA. The yield in both cases is higher than 90%.

The copolymer with an equimolar feed molal ratio was completely insoluble in water. This was due to the electrostatic interaction between the sulfonate and ammonium groups yielding an inter- or intrapolymer complex. This complex will be neutral with probable crosslinked points, hence the nonsolubility in water. It could also occur with the other copolymers but it was not observed, because the two copolymers are completely soluble in water.

On the other hand, copolymers containing ammonium and carboxylic groups were synthesized (Table I). The copolymer composition was determined through the ^{1}H-NMR spectra by a comparison of the integration area of the characteristic proton signal of
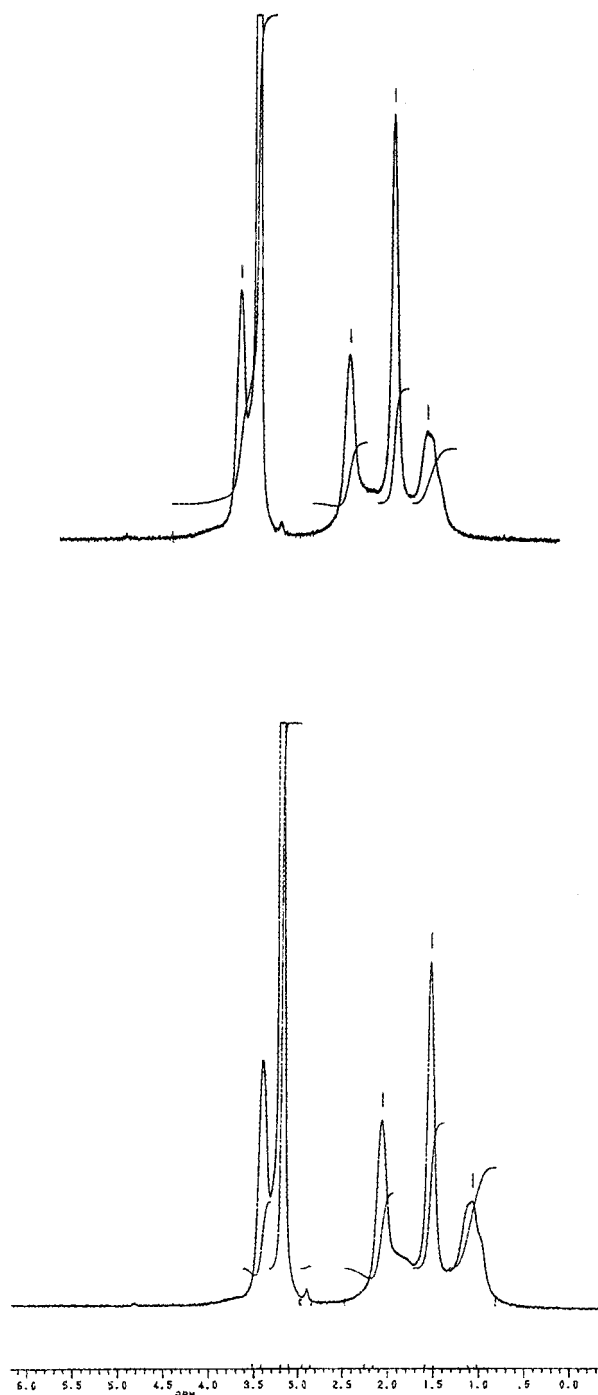
II. For the PMPTA-*co*-MA copolymers, only fractions above 100,000 *D* were obtained.

We can observe that the M_w values determined on the fractions deviate slightly from the nominal values defined by the exclusion limits of the membranes used to fractionate. Thus, in these fractions there is a general shift of their M_w toward higher values than those delimited by the exclusion limits of the membranes. In spite of this shift toward higher M_w values, we can see that the fractionation processes have been effective in separating the ranges of molecular weights. The values of the M_w for all the fractions correlate well with the ranges defined by the exclusion limits of the ultra-filtration membranes, and there is no interchange or overlap between consecutive ranges.

The polymer–metal ion interaction was studied by the LPR technique. With this technique it is possible to obtain the retention profiles, that is, the retention (*R*) versus filtration factor (*Z*). Here *Z* is defined as the ratio between the volume filtrate (V_f) and the volume in the cell (V_0) and *R* is the fraction per unit of metal ions remaining in the cell, which is normally expressed as a percentage. Figure 2 shows the retention profile for PMTA. There is practically no retention for all of the metal ions except Ag(I). This is due to the electrostatic repulsion between the cationic group of the polymer and the cationic metal ions. Silver ions are retained because the counterion of the polycation is chloride; therefore, an AgCl precipitate is formed. On the other hand, the retention capacity for the copolymers is dependent on the copolymer composition. It is clearly shown in Figure 3 that, when the copolymer is richest in MPTA comonomer, the retention behavior is very similar to the homopolymer PMPTA, and when the copolymer composition is richest in APSA comonomer, the retention behavior is very similar to
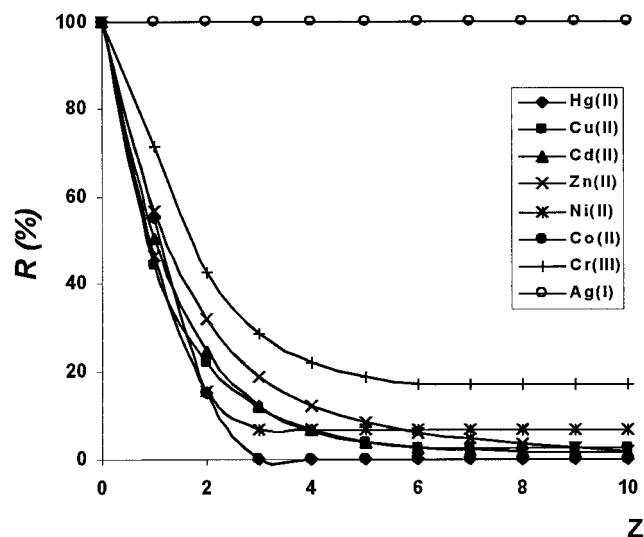

Figure 1 The ¹H-NMR spectra of P(MPTA-*co*-APSA)21 (top) and P(MPTA-*co*-APSA)12 (bottom) at 250 MHz with D₂O TMS as a solvent at room temperature.

each monomer. The copolymer with an equimolar feed mole ratio was insoluble in water.

All the water-soluble copolymers were purified and fractioned through ultrafiltration membranes with molecular weight cutoffs of 3,000, 10,000, 30,000, and 100,000 g mol⁻¹. All fractions were lyophilized.

The weight-average molecular weight (M_w) for all products and fractions obtained are presented in Table

Figure 2 The retention profile of PMPTA at pH 3 for all the metal ions under studied.
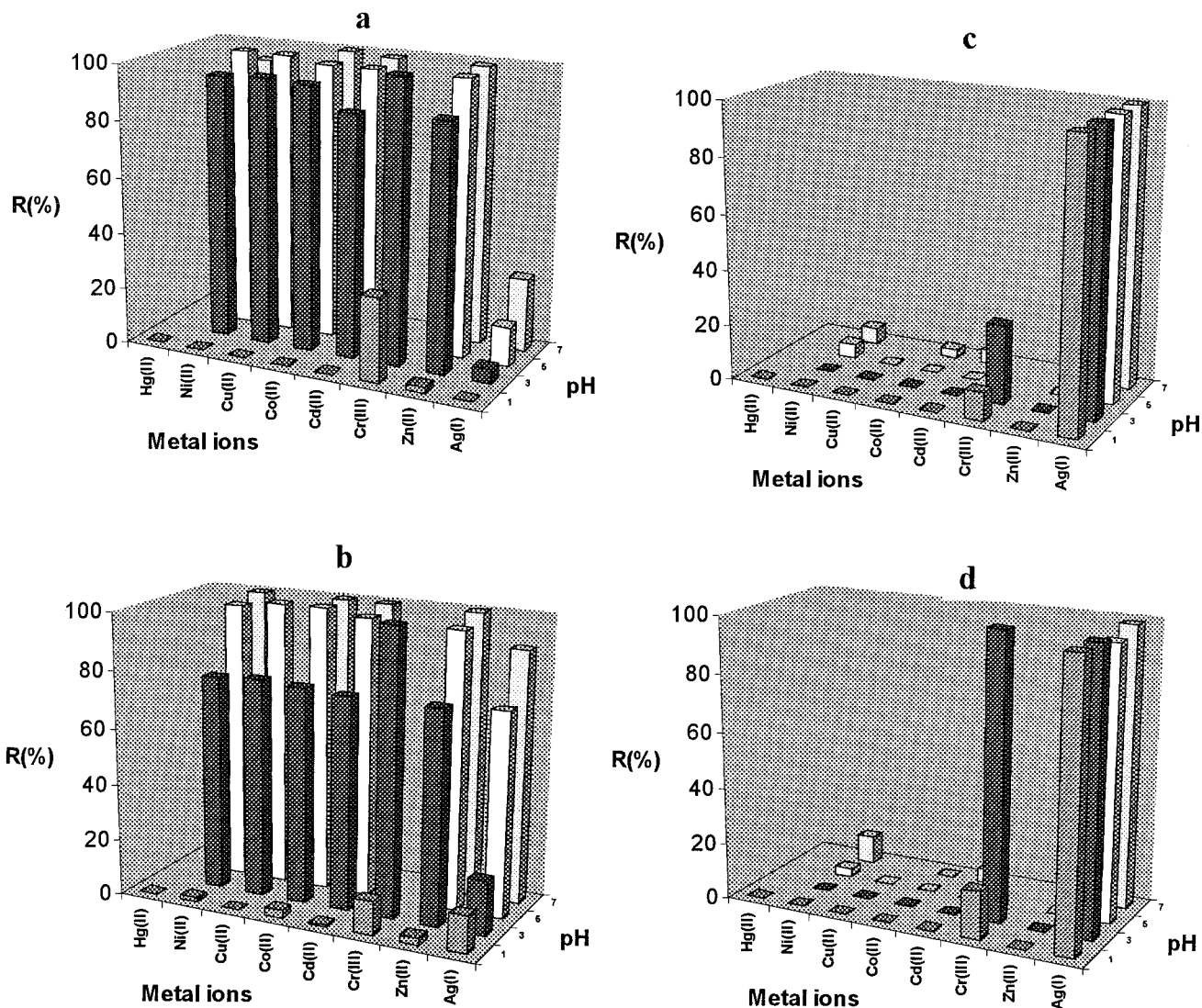
COPOLYMERS WITH OPPOSITE CHARGED COMONOMERS

Figure 3 The retention behavior at $Z = 10$ of different metal ions for (a) PAPSA, (b) P(MPTA-*co*-APSA)12, (c) PMPTA. and (d) P(MPTA-*co*-MA)21 at different pH values.

the homopolymer PAPSA. In the latter case, the Ag(I) retention is higher in the copolymer because two comonomers are interacting with the silver ions. PAPSA interacts electrostatically and MPTA through the chloride counterion.

Moreover, the polymer–metal ion interaction is dependent on the pH, which is basically due to the protonated and deprotonated equilibrium of the sulfonic and carboxylic acid groups.

The LPR method is also able to predict the force of the interaction between the polymer and metal ions. It is possible to plot the differential of the retention with respect to the filtration factor (Fig. 4). At pH 1 for all metal ions, the change of the retention with respect to Z is greater. This is due to the fact that the retention at $Z = 0$ is always 100%, which means the polymer–metal ion interaction is weak; at $Z = 5$, the metal ions have passed completely form the cell through the

ultrafiltration membrane. At higher pH the change of the retention in the function of Z is practically zero for all the metal ions. This means that the polymer–metal ion interaction is very strong and the amount of metal ions in the cell stays constant in the entire range of filtration factors. If we compare the polymer–metal ion interaction force at pH 3, it is possible to establish the following sequence:

$$M^{3+} > M^{2+} > M^{+}$$

This behavior is in agreement with the electrostatic force, because this depends on the ions' charge.

CONCLUSION

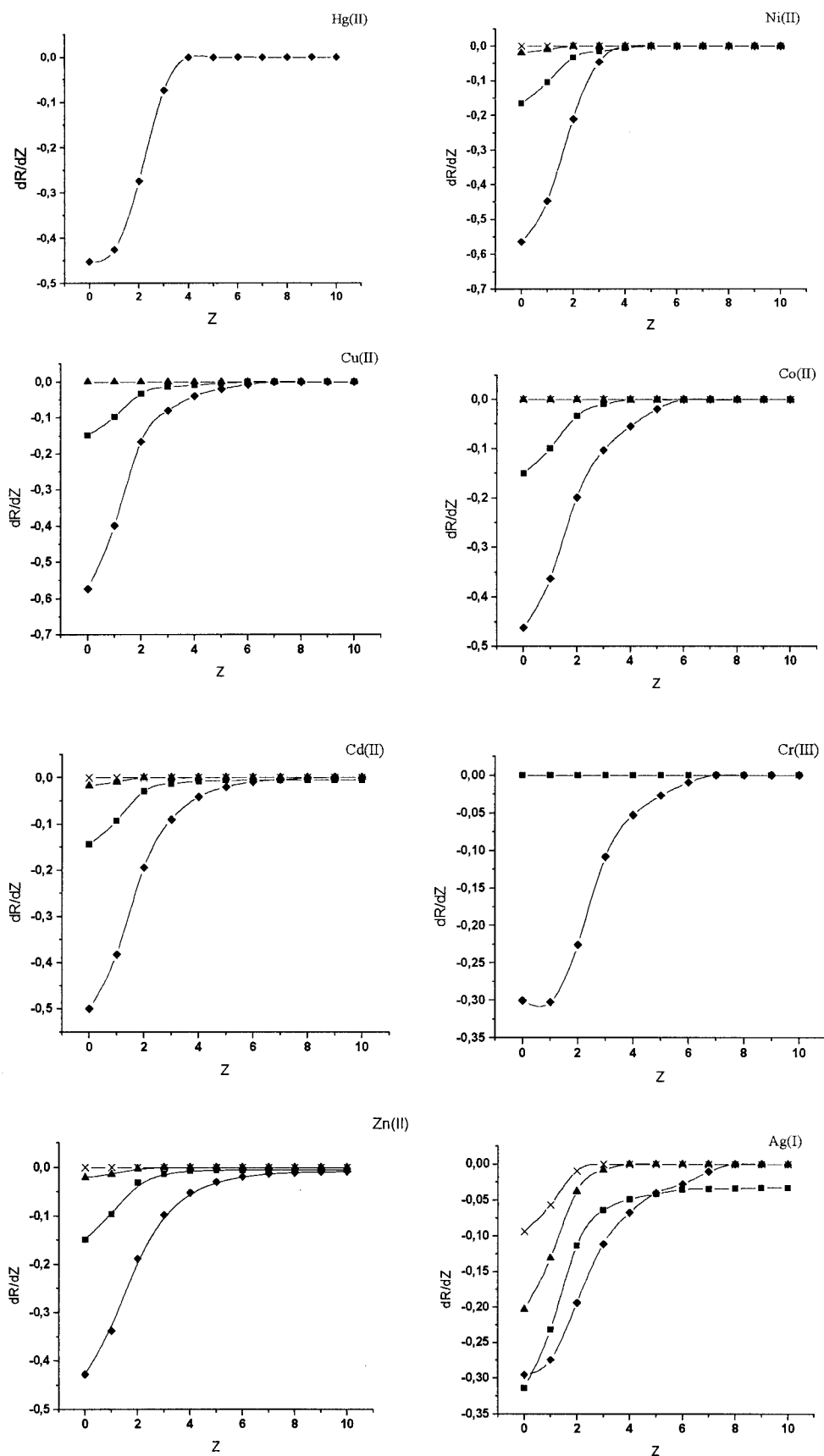Water-soluble polymers containing ammonium, sulfonic, and carboxylic moieties were synthesized by

Figure 4   The differential retention as a function of the filtration factor for the polychelatogens P(MPTA-*co*-APSA)12 at (◆) pH 1, (■) pH 3, (▲) pH 5, and (×) pH 7.

radical polymerization and their ability to bind metal ions by the LPR technique was studied. The polymer–metal ion interaction was strongly dependent on the pH, ligand group, and charge of the metal ions. The carboxylic groups form complexes with the metal ions, but the sulfonic groups interact through basically electrostatic forces.

References

1. Warshawsky, A.; Marques, G.; Kahana, N.; Kampel, V.; Bourdelande, J. L.; Valiente, M. Macromol Chem Phys 2001, 202, 2659.
2. Dominguez, L.; Benak, K. R. J Econ Polym Adv Technol 2001, 12, 197.
3. Beauvais, R. A.; Alexandratos, S. D. React Polym 1998, 36, 113.
4. van der Water, L. G. A.; ten Hoonte, F.; Driesse, W. L.; Reedjik, J.; Sherrington, D. C. Inorg Chim Acta 2000, 303, 77.
5. Rivas B. L. In Polymeric Materials Encyclopedia. Synthesis, Properties and Applications; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 6, p 4137.
6. Geckeler, K. E.; Lange, G.; Eberhardt, H.; Bayer, E. Pure Appl Chem 1980, 52, 1883.
7. Spivakov, B. Ya.; Geckeler, K.; Bayer, E. Nature 1985, 315, 313.
8. Spivakov, B. Ya.; Shkinev, V. M.; Geckeler, K. E. Pure Appl Chem 1994, 66, 631.
9. Geckeler, K. E.; Rivas, B. L.; Zhou, R. Angew Makromol Chem 1991, 193, 195.
10. Geckeler, K. E.; Zhou, R.; Rivas, B. L. Angew Makromol Chem 1992, 197, 107.
11. Geckeler, K. E.; Zhou, R.; Fink, A.; Rivas, B. L. J Appl Polym Sci 1996, 60, 2191.
12. Palmer, V.; Zhou, R.; Geckeler, K. E. Angew Makromol Chem 1994, 215, 175.
13. Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. J Polym Sci Part A Polymer Chem 1997, 35, 2461.
14. Rivas, B. L.; Moreno-Villoslada, I. J Phys Chem B 1998, 102, 6994.
15. Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. J Appl Polym Sci 1999, 72, 741.
16. Rivas, B. L.; Moreno-Villoslada, I. Polym Bull 2000, 44, 159.
17. Rivas, B. L.; Pereira, E. Bol Soc Chil Quím 2000, 45, 165.
18. Rivas, B. L.; Moreno-Villoslada, I. Chem Lett 2000, 166.
19. Rivas, B. L.; Moreno-Villoslada, I. J Membr Sci 2000, 178, 165.
20. Rivas, B. L.; Pooley, S. A.; Luna, M. Macromol Rapid Commun 2000, 13, 905.
21. Rivas, B. L.; Martínez, E.; Pereira, E.; Geckeler, K. E. Polym Int 2001, 50, 456.
22. Rivas, B. L.; Pooley, S. A.; Luna, M. Macromol Rapid Commun 2001, 22, 418.
23. Rivas, B. L.; Pereira, E. D.; Horta, A.; Renamayor, C. S. Eur Polym J, submitted.