

# Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine]: An Efficient Water-Soluble Polymer for Selective Separation of Metal Ions

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**ABSTRACT:** Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine], obtained by spontaneous copolymerization, which contains different types of ligand groups as tertiary amines and hydroxyl and amide groups, was tested as a polychelatogen using the liquid-phase polymer-based retention (LPR) technique. The metal ion retention ability of this polymer was found to depend on the pH and it showed a high selectivity to copper(II) at pH 5. The maximum capacity of Cu(II) was determined at pH 5 by using the enrichment variant of LPR. The retention capacities of the polymer with Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) were studied at different pH and the results are compared with those of branched polyethylenimine and poly[1-(2-hydroxyethyl)aziridine] homopolymers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 817–824, 1998

**Key words:** water-soluble polymers; spontaneous copolymerization; metal ions; separation

## INTRODUCTION

Polymers with complexing properties have gained considerable importance in terms of their potential applications in separation science. Besides investigations on the complexation of metal ions by insoluble resins,<sup>1–5</sup> hydrophilic polymers have found great interest as supports for chelating groups. Many water-soluble polymer types have been synthesized by homo- and copolymerization as well as by polymer-analogous reactions.<sup>6–10</sup> These water-soluble polymers with the ability to chelate metal ions are named polychelatogens. A number of techniques have been described<sup>6,11,12</sup> to recover metals from water using water-soluble polymers. The liquid-phase polymer-based reten-

tion (LPR) technique used in this work was recently approved by the IUPAC.<sup>13</sup> This technique uses solutions of polychelatogens in combination with membrane filtration in which selective separation of metal ions can be achieved.<sup>6,14</sup> Metal ions with high interaction rates with the polymer stay retained by the polymer while other ions are eluted through the ultrafiltration membrane. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile for the retention of the different metal ions by the polychelatogen during filtration can be obtained. This technique also allows the calculation of the maximum capacities of polymers for a metal ion.<sup>6</sup>

Many authors have reported the synthesis of copolymers in the absence of an initiator, catalyst, or high radiation energy.<sup>15–19</sup> The copolymerization reaction occurs by interaction of a nucleophilic monomer with an electrophilic one. The resulting “genetic zwitterion” is then responsible for both initiation and propagation reactions.

This article reports the use of a polymer ob-

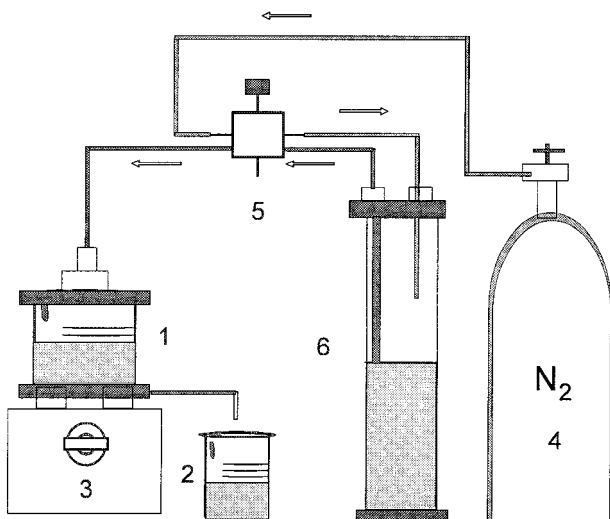
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**Figure 1** Retention unit: (1) filtration cell containing the polymer-metal complex; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.

tained by spontaneous copolymerization as poly-chelator using the LPR technique. The metal ion retention ability for Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) was studied at different pH strengths.

## EXPERIMENTAL

### Materials

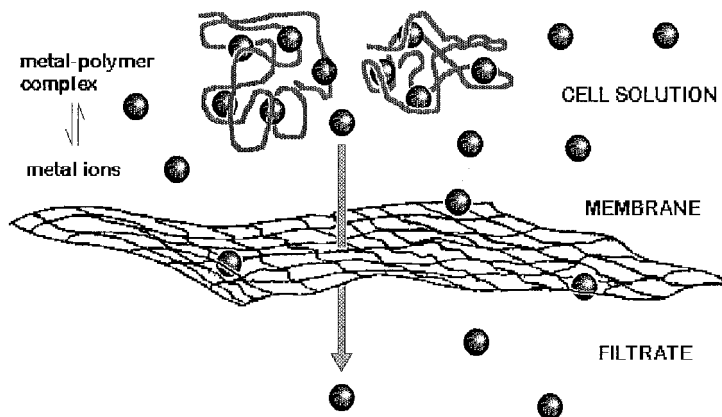
Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] was obtained by spontaneous copolymerization.<sup>20</sup> Poly[1-(2-hydroxyethyl)aziridine] was obtained by cationic polymerization of 1-(2-hydroxyethyl)-

aziridine (Aldrich) using borontrifluoride etherate (1 mol %) as the initiator; the product had a viscosity of 0.222 g/dL.<sup>21</sup>

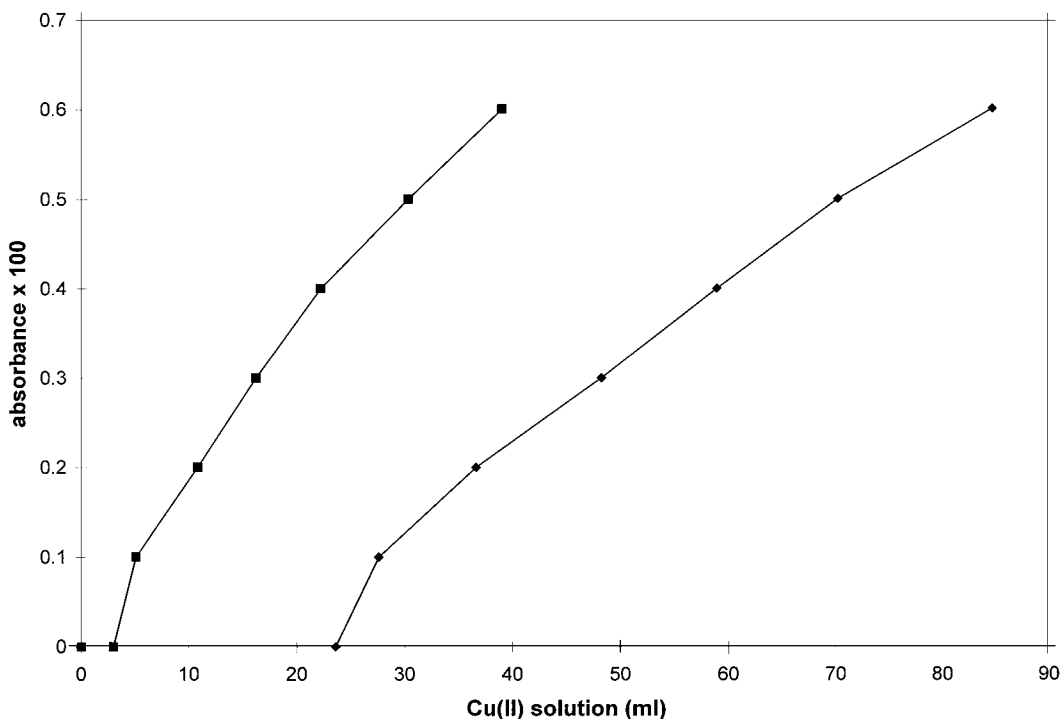
The purified polymers were dissolved in water and fractionated by ultrafiltration over three membranes with an exclusion rating of 3000, 10,000, or 100,000 g/mol (Filtron), respectively. Water was eliminated by lyophilization and three fractions were obtained corresponding to the following molecular weight ranges: 3000–10,000, 10,000–100,000, and over 100,000 g/mol. Metal standard solutions of 1,000  $\mu\text{g/mL}$  purchased from Merck were used to prepare metal-ion solutions of 100  $\mu\text{g/mL}$ .

### LPR Technique

The unit used for retention studies consisted of a filtration cell with a magnetic stirrer and a membrane with an exclusion rating of 10,000 g/mol (Filtron), a reservoir, a selector, and a pressure source (see Fig. 1). The LPR technique is based on the separation of ions bound to water-soluble polymers with chelating or ion-exchange groups from non-bound ions (see Fig. 2). With the aid of the pressure source and the reservoir solution, a continuous flow of liquid is established through the cell, keeping constant the total volume of liquid in it. The ultrafiltration cell membrane had a known exclusion rating which permits water and noncomplexed metal ions to pass through it due to their small molecular size. On the other hand, the polymeric species, precursor polymer, and polymer-metal complexes, with a substantial larger size than the membrane pores, are retained in the cell solution. In the enrichment variant of this technique, the precursor poly-



**Figure 2** Principle of the LPR technique.



**Figure 3** Chelation of Cu(II) at pH 5: (— ■ —) reference solution; (— ◆ —) polymer solution.

mer is placed in the cell, and a metal-ion solution contained in the reservoir is passed through the cell. In the elution variant, the precursor polymer and a mixture of different metal ions are placed in the cell and the mixture is eluted with water stored in the reservoir.

Metal-ion concentrations of the filtrate were measured by atomic absorption on a Perkin–Elmer 3100 spectrometer. The pH was controlled on a pH meter of H. Jürgens & Co. A Dr. Lange Cadas 100 spectrophotometer was used for UV-vis measurements.

#### Maximum-Capacity Studies

Poly[acrylamide-*co*-1-(2-hydroxyethyl)aziridine] (1.08 mmol; fraction over 100,000 g/mol) was dissolved in bidistilled water, and after adjusting the pH to pH 5, the solution was brought to 20 mL of total volume and placed into the cell. The cell membrane had an exclusion rating of 10,000 g/mol. A solution of  $\text{Cu}(\text{NO}_3)_2$  (3.16  $\mu\text{mol}/\text{mL}$ ) was passed through the cell from the reservoir under a total pressure of 3 bar, keeping constant the total volume in the cell to 20 mL, and the filtrate was analyzed by visible spectrophotometry at  $\lambda$  of 780 nm.

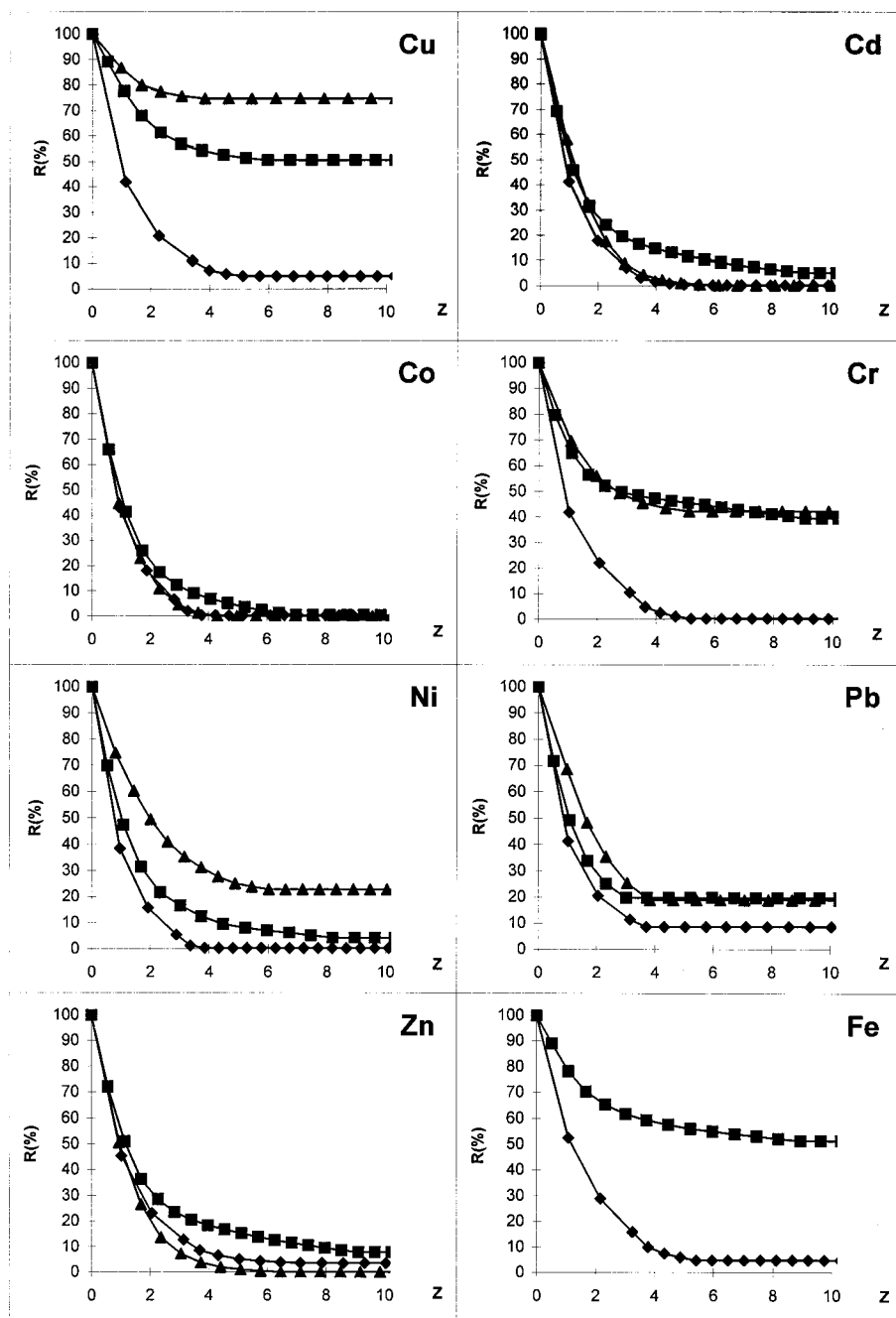
#### Retention Studies

Poly[acrylamide-*co*-1-(2-hydroxyethyl)aziridine] (1 mmol; fraction over 100,000 g/mol) and  $\text{NaNO}_3$  (255 mg) were dissolved in bidistilled water, and metal solutions (400  $\mu\text{g}$  of each metal ion) were added. The solution was brought to 20 mL of total volume, and after adjusting the pH, it was left overnight. The pH of the cell and the reservoir solutions were adjusted to the same value. The filtration runs were carried out over a membrane with an exclusion rating of 10,000 g/mol under a total pressure of 3 bar, keeping constant the total volume in the cell to 20 mL. Filtration fractions were collected and the metal concentrations were analyzed. The metal ions studied were Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II). Fe(II) was not used at pH over 3 because it is susceptible to precipitate.

## RESULTS AND DISCUSSION

#### Maximum Capacity of Cu(II)

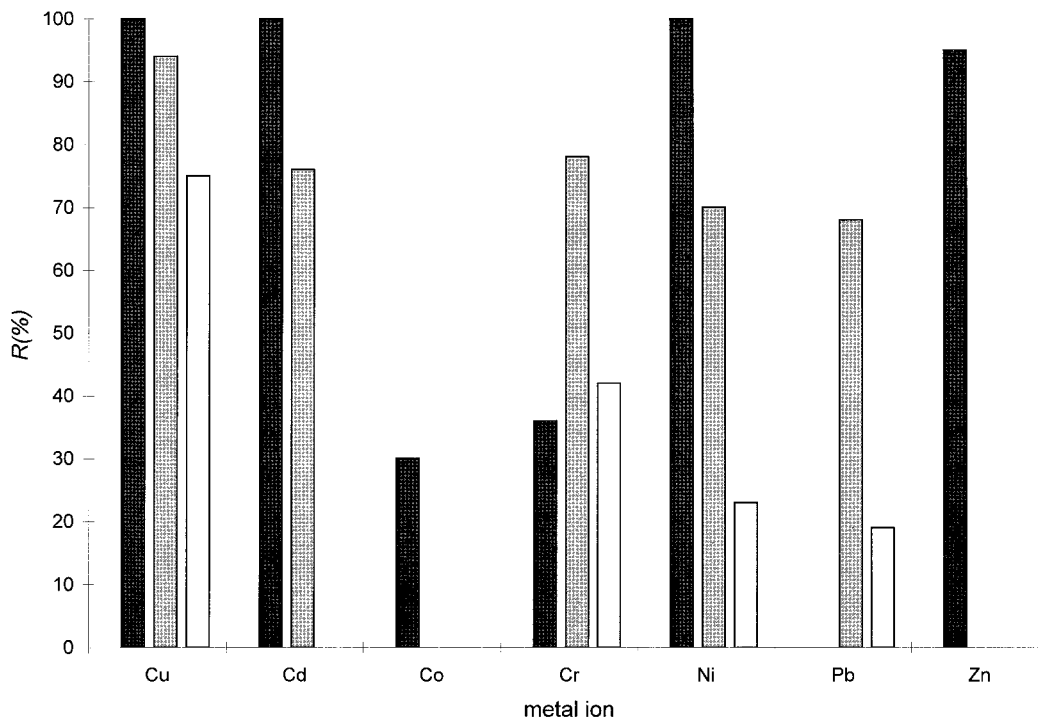
Figure 3 shows the measurements of the absorbance at  $\lambda$  of 780 nm of the filtrate versus the



**Figure 4** Retention profiles of Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) using poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] as polychelator. Absolute polymer amount: 1.0 mmol. Absolute metal ions amounts: 400  $\mu\text{g}$  of each metal species. (—  $\blacklozenge$  —) pH 1; (—  $\blacksquare$  —) pH 3; (—  $\blacktriangle$  —) pH 5.

volume of the Cu(II) solution passed through the membrane from the reservoir. Two curves are shown, corresponding to the polymer solution and to the reference solution (20 mL of water). The maximum capacity ( $C$ ) is given by the break of

the curves as it has been previously defined.<sup>6</sup> To that point, all the Cu(II) from the solution passed through the cell has been retained by the polymer. Thus, the maximum capacity calculated from these data is 0.4 mmol Cu(II)/g polymer, since



**Figure 5** Retention capacities of Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) using (■) polyethylenimine, (▨) poly[1-(2-hydroxyethyl)aziridine], and (□) poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] as polychelators at pH 5.

21 mL of the 3.16 mM Cu(II) solution has passed through the cell solution containing 170 mg of polymer. The dimensionless enrichment factor ( $E$ ) is defined<sup>6</sup> as

$$E = C[P]/[M]_0 = V_f^{\text{sat}}/V_0 \quad (1)$$

where  $C$  is the maximum capacity;  $[P]$ , the polymer concentration in g/L;  $[M]_0$ , the concentration of the metal solution;  $V_f^{\text{sat}}$ , the total volume of the filtrate when the saturation of the polymer is achieved; and  $V_0$ , the volume of the polymer solution in the cell. The filtration factor ( $Z$ ) is defined as the volume ratio of the filtrate ( $V_f$ ) versus the volume in the cell ( $V_0$ ). So,  $E$  can be defined as the filtration factor in conditions of saturation of the polymer, that is,  $E = Z^{\text{sat}}$ . The value of  $E$  of Cu(II) calculated for this polymer is  $E = 1.1$ .

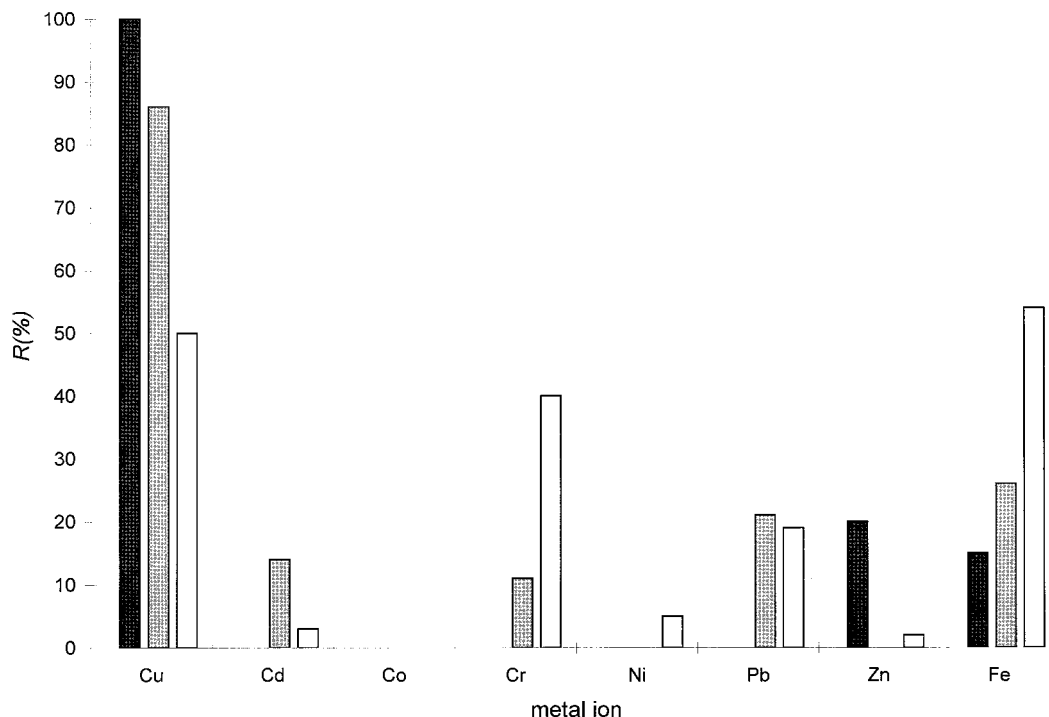
### Metal-Ion Retention Capacities

Typical retention profiles are shown in Figure 4, where retention ( $R\%$ ) versus the filtration factor ( $Z$ ) is plotted as a function of the pH.  $Z$ , as ex-

plained above, is defined as the volume ratio of the filtrate ( $V_f$ ) versus the volume in the cell ( $V_0$ ) and  $R$  is the fraction per unit of metal ions remaining in the cell. The solution mixture turns blue with increase of the pH. In this case, the retention profile at pH 7 is not shown because at pH values over 6 a precipitate appeared.

At  $Z$  values high enough, a remaining residue of metal ions is frequently found which cannot be eluted by filtration at the same pH conditions. This remaining percentage is called the retention capacity of a polymer. The retention capacities of different polymers may be compared to obtain the relative selectivities.

In Figure 5, it is shown the comparison of the retention values at  $Z = 10$  and pH 5 for branched polyethylenimine<sup>9</sup> (BPEI) and poly[1-(2-hydroxyethyl)aziridine]<sup>8</sup> (PHEA), with poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] (AAM-HEA). PHEA loses its retention capacity for Zn(II) and to some extent for Ni(II) with respect to BPEI, and the retention capacity for Cr(III) increases. AAM-HEA becomes more selective for Cu(II) with respect to the PHEA losing its binding capacity for Cr(III),



**Figure 6** Retention capacities of Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) using (■) polyethylenimine, (▨) poly[1-(2-hydroxyethyl)aziridine], and (□) poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] as polychelating agents at pH 3.

Co(II), Ni(II), and Pb(II) and presenting no retention of Cd(II) at all. That makes AAm-HEA highly selective for Cu(II) at this pH value.

The situation is very different at pH 3 as shown in Figure 6. In this case, BPEI presents the highest selectivity for Cu(II). The PHEA homopolymer is also quite selective for Cu(II), while the copolymer loses selectivity and has an important retention capacity for Cu(II), Cr(III), and Fe(II). Both PHEA and BPEI do not retain Cr(III) or Fe(II).

### Structural Considerations

The ability of molecules to form complexes with metal ions depends on several variables, such as charge/radius ratio, charge distribution, polarization of both ligands and the central atom, and the possibility of chelate formation. The ionic radius of Cu(II) is relatively small in comparison with that of Cd(II) or Pb(II), but does not differ much from that of Co(II), Zn(II), or Ni(II).

The ability of polyethylenimine to form complexes with metal ions is well known.<sup>9</sup> Its complexing properties depend essentially on the mi-

crostructure. Commercially available water-soluble polyethylenimine (**1**) is a branched polymer with primary, secondary, and tertiary amino groups (see Fig. 7).

Contrarily, poly[1-(2-hydroxyethyl)aziridine] (**2**) is characterized by tertiary amine moieties at the polymeric backbone and a hydroxy group at the side chain (see Fig. 7). The copolymerization of the 1-(2-hydroxyethyl)aziridine with acrylamide results in a polymer (**3a**, **3b**) whose two possible proposed structures are shown (see Fig. 7).<sup>20</sup>

On the other hand, the amido groups are not strong complexing ligands. Polyacrylamide does not retain any of the metal ions studied.<sup>22</sup> These observations are in concordance with the studies made by Hamaya and Hiratani.<sup>23</sup> The same retention profiles are found for the polymers poly[1-(2-hydroxyethyl)aziridine] and poly[2-methyl-2-oxazoline-co-1-(2-hydroxyethyl)aziridine] (**4**) made by Geckeler et al.,<sup>24</sup> which may indicate the nonparticipation of the amido group in the chelation process (see Fig. 7). In the case of the AAm-HEA copolymer, it is evident that the acrylamide plays an important role in the polychelating properties of the polymer, in view of

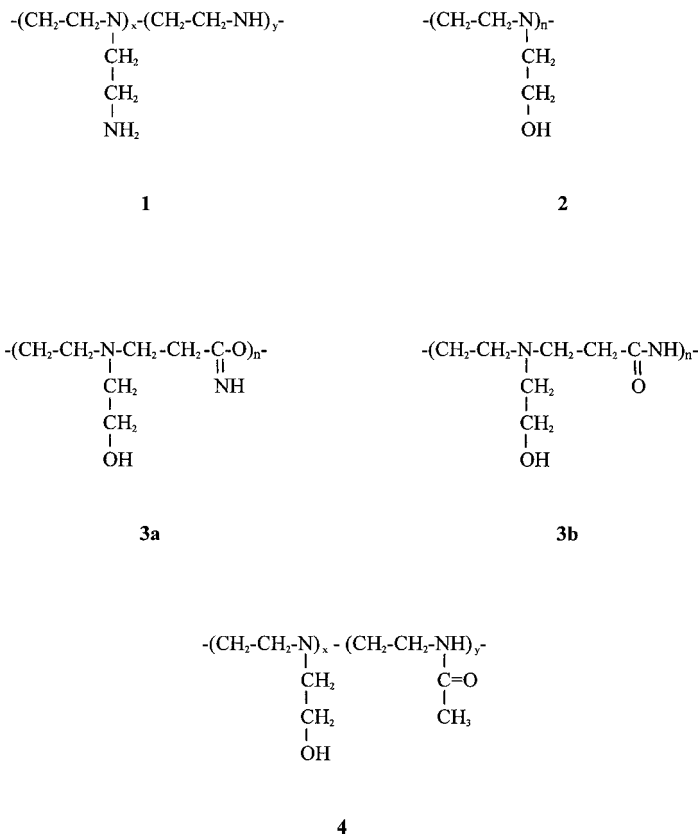


Figure 7 Structures 1-4.

the differences found between the copolymer and the PHEA homopolymer. It is possible to think that these differences might be attributed to structural considerations. The alternating character of the polymer may diminish the possibility of chelate formation due to the higher distance between the ligand groups. Further investigations on the structure of the AAm-HEA copolymer are needed.

## CONCLUSIONS

Liquid-phase polymer-based retention (LPR) is an accurate technique for the separation of metal ions. A selective separation of Cu(II) from other metal ions may be carried out by the poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] copolymer obtained by spontaneous copolymerization, at pH 5, while branched polyethylenimine is more suitable at pH 3. Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] retains Cu(II), Cr(III), and Fe(III) at pH 3. The selective properties of the copolymer are better than

those of the poly[1-(2-hydroxyethyl)aziridine] homopolymer. The maximum capacity of the poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] copolymer is 0.4 mmol Cu(II)/g polymer for this metal ion.

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