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Application of a synthetic water-soluble poly(*N*-maleyl glycine-*co*-acrylamide) as polychelatogen for inorganic ions in aqueous solutions

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Summary

The water-soluble poly(N-maleyl glycine-*co*-acrylamide) (P(MG-*co*-Am)) reagent with strong complexing properties for the inorganic ions Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), Pb(II), Hg(II), As(V), and Se(IV) was investigated in aqueous phase in conjunction with membrane filtration using the Liquid-phase Polymer-based Retention (LPR) technique. The P(MG-*co*-Am) was shown to be useful for retention of different inorganic ions and their separation from elements not bound to the polymeric reagent. The inorganic ion interaction with the hydrophilic polymer was determined as a function of pH and filtration factor. At higher pH, the copolymer can be applied to the separation and preconcentration of most of the inorganic ions. Viscosimetric measurements of the copolymers were performed in the presence of metal ions at different pH values.

Introduction

The poly(N-maleyl glycine-*co*-acrylamide) (P(MG-*co*-Am)) is a water-soluble copolymer (1) included in the class of synthetic polyelectrolyte polymers that combine both acidic and basic groups in the same chain called polyampholytes (2,3). These polymers can form complexes with noble metals and some rare metals (4).

The study of the physico-chemical properties of this class of copolymers provides an approach to the analysis of the intramolecular forces originating from the electrostatic attraction of the acidic and basic groups and elucidating their influence on the conformational properties of macromolecules.

As a consequence of the nonionic character of poly (acrylamide), its viscosity remains constant with a change of pH from 0 to 10; at pH > 10, the polymer undergoes hydrolysis and the specific viscosity increases sharply. The presence of amide and carboxyl groups at the chains of the dry polymer must lead to an intense intermolecular interaction at the expense of hydrogen bond between the chains which are destroyed by salts.

The poly(N-maleyl glycine-*co*-acrylamide) with a copolymer composition 1:1 had been previously synthesized and characterized (1). It contains monomeric units, situated alternatingly along the chain with a weakly acidic group and an amidic group. As a consequence of the nonionic character of poly(acrylamide) these polymers possess an overall positive charge at low pH values, and a negative charge at high pH values. The presence of amide and carboxyl groups in the polymer chains must lead to an intense intermolecular interaction at the expense of hydrogen bonds between the chains (5).

Polymers as metal ion-complexing agents have been extensively studied (6-8). Hydrophilic polymers with complexing groups (polychelatogens) have been tested to show the applicability of the method to separate various metal cations and anionic species for analytical and technological purposes. This method, based on the retention of certain ions by a membrane which separates low molar mass compounds from macromolecular complexes of ions, is called Liquid-phase Polymer-based Retention (LPR) (9-13).

This paper reports the interaction of water-soluble poly(N-maleyl glycine-*co*-acrylamide) with different inorganic ions in aqueous solution in conjunction with membrane filtration varying the pH and the filtration factor.

Experimental

Reagents and Equipments.

Chemicals: Were purchased from Fluka and Merck p.a. grade.

Polychelatogen: Poly(N-malcyl glycine-*co*-acrylamide), P(MG-*co*-Am), was synthesized by radical copolymerization with: 1:1 monomer composition in solution using 0.5 mol% of AIBN as the initiator (1). Prior to the interaction studies, the polymer was dissolved in water and purified by membrane filtration using a membrane with an exclusion limit of a molecular weight of 10.000 g/mol. The yield of the copolymer was higher than 90%. All salts were of analytical grade and used as received.

Complexation procedure: For the determination of the complex binding capacity, the copolymer (200 mg) was dissolved in water (10 mL) and adjusted to the corresponding pH by addition of diluted nitric acid or sodium hydroxide. The aqueous solutions of polymer and metal nitrates chlorides, (20 ppm) or oxides (As_2O_5, SeO_2,40 ppm) (2 wt%) solution were placed into the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water adjusted to the same pH as that of the cell solution. A membrane with an exclusion limit of 10.000 g/mol (AMICON PM 10 or equivalent) was used. The system was pressurized (300 kPa), the cell solution stirred for 10 min and then washed with the reservoir fluid at a flow rate of 4-6 mL/min. The filtration fractions (Z = 10) were collected and the concentrations of metal ions in the filtrate and the retentate were determined by atomic absorption spectroscopy. The copolymer was lyophilized for further analytical control. Retention values were calculated from the ion-concentration measurements of filtrate and retentate.

Equipment: The determination of the metal ion concentration content in the filtrates was carried out with a Perkin-Elmer 1100 Atomic Absorption Spectrometer. Viscosimetric measurements were performed with an Ostwald viscosimeter. For lyophilization a continuous freeze dryer (New Brunswich Scientific Co) was used. The pH was determined with a Metrohm pH-meter E 512. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelatogen P(MG-*co*-Am). Details have been described previously (14-17).

Results and discussion

Polymers such as poly (ethyleneimine), poly(vinyl pyrrolidone), poly(acrylamide) and other widely used were previously applied to the concentration and separation of various elements in the form of neutral salts (10,11).

The poly(MG-*co*-Am) copolymer is obtained from counits which have the characteristic of electrolyte (MG) and non-electrolyte (Am). The complexation properties of P(MG-*co*-Am) were investigated by using LPR technique at pH 3, 5, and 7 with eight metals and two non-metal ions.

The retention of metal ions in the cell solution is defined as:

$$R = C_r C_o^{-1} 100 (\%)$$

where C_r is the metal ion concentration in the retentate (the cell solution after a filtrate volume of V_f has been passed) and C_o is the initial metal ion concentration in the cell. The filtration factor Z, expressed in relative units, is another convenient characteristic of the process (15, 16-18):

$$Z = V_f \bullet V_c^{-1}$$

where V_f and V_c correspond to the volume in the filtrate and in the cell respectively.

The retention depends on polymer complex dissociation which is generally described by a reversible reaction:

$$M + L \Leftrightarrow ML$$

In systems with inorganic ion concentrations which are small in respect to the polymer concentration, only the formation of ML may be taken into account.

We have previously reported the ability binding of both homopolymers for these metal cations. The amido groups are not strong complexing ligands, therefore poly (acrylamide) does not retain any of the metal ions studied (18). These results are in agreement with the studies made by Hiratani (19). Poly(N-maleyl glycine) shows only a strong complexation at pH 5. A complete retention was observed for Co(II), Cd(II), Zn(II), and Cr(III). The retention capability for Cd(II), Co(II), Ni(II), Zn(II) decreases close to 50% at pH 3.0 (17).

Typical retention profiles of P(MG-*co*-Am) are shown in Figs. 1 and 2. In general, a high complexation with P(MG-*co*-Am) takes place with all metal ions at pH 3, 5 and 7, except at pH 3 for Ni(II) and Co(II), where the retention values are 50%. These values increased at pH 5 and 7, respectively (see Table 1). A predominant influence of the complexing comonomer units at pH 5 and 7 was not observed. The retention values of the metal were lightly increased from pH 3. This could explain the positive interaction with the metal-ions at pH 5 and 7. All the other metal ions did not show a strong dependence of the pH and filtration factor Z. For example, at pH 3 for a filtration factor of Z = 10, Zn(II) showed a retention value over 90% and Cr(III) and Cu(II) of 86.5% and 85.5% respectively (see Table 1). At pH 5 and 7 all the retention values are over 85%, except for Hg(II), 80% retention. Thus, P(MG-*co*-Am) is an effective reagent for separation of various metal ions, including Hg(II) and Pb(II). This polymer retains Hg(II) and Pb(II) at different pH values, but the retention of both cations Hg(II) and Pb(II) is decreased by effect of the presence of the metal ions such as Zn(II), Cd(II)m Ni(II), Cu(II), Co(II), and Cr(III) (see Fig. 1) compared to that when they are found in a mixture with Se(IV) and As(V) (see Fig. 2). It has been also reported that PEI and PVP polychelatogens are effective reagents for the separation of Hg(II) and noble metals from other elements at pH 1 (20).

The differences in the complexing ability of the copolymer in respect to the homopolymer poly(N-maleyl glycine) previously reported (17, 21) may be attributed primarily to the structural difference in the comonomer repetitive unit. The main reason is that the P(MG-*co*-Am) has a structure with three different functional groups.

Assuming that the carboxylic acid moiety interacts stronger than does the tertiary amide moiety, each metal ion (divalent) such as Co(II) ion interacts with one, two, or four carboxyls:

$$\mathrm{R\,COOH} + \mathrm{M}^{2+} \xrightleftharpoons{K_1} \mathrm{R\,COO^{-}M^{+}} + \mathrm{H}^{+}$$

$$\mathrm{R\,COO^{-}\,M^{+}} + \mathrm{RCOOH} \xrightleftharpoons{K_1} \mathrm{(RCOO)_2M} + \mathrm{H}^{+}$$

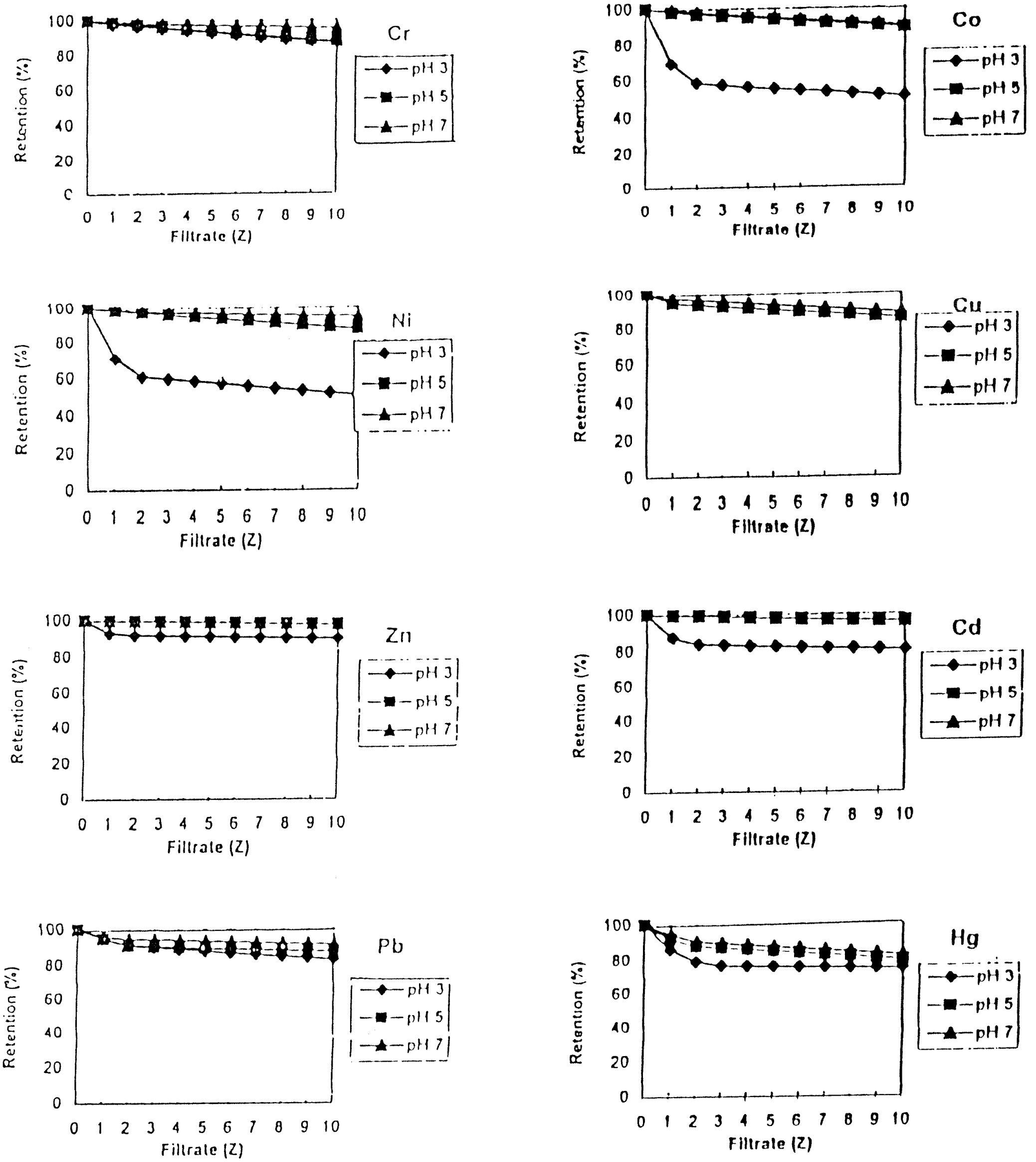

Figure 1. Percentage of retention (R%) of Cr(II), Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Pb(II), and Hg(II) ions by an aqueous solution of poly(maleyl glycine-*co*-acrylamide) at pH 3, 5, and 7.

The products of the composition 2:1 are presumably formed. It may be achieved either by interaction with two carboxyls of the same polymer chain (intramolecular interaction or by a different one, intermolecular interaction) (22). At lower pH the ion exchange process is favored but as increases the degree of ionization of polychelatogen, the interaction among the carboxylate moieties with the metal ions is favored. Therefore, the retention of metal ions increases significantly, particularly for Co(II) and Ni(II) by an increase of the pH.

Table 1. Retention (%) of eight metal ions by poly(N-maleyl glycine-*co*-acrylamide), at pH 3, 5, and 7. Filtration factor (Z) = 10.

Metal		R (%)	
Ion	pH 3	pH 5	pH 7
Cr(III)	86.5	87.5	89.3
Co(II)	50.0	88.8	90.0
Ni(II)	50.7	87.0	89.3
Cu(II)	85.5	85.4	88.6
Zn(II)	90.1	97.5	97.5
Cd(II)	80.5	96.0	96.0
Pb(II)	83.0	87.7	91.8
Hg(II)	74.8	80.0	82.5

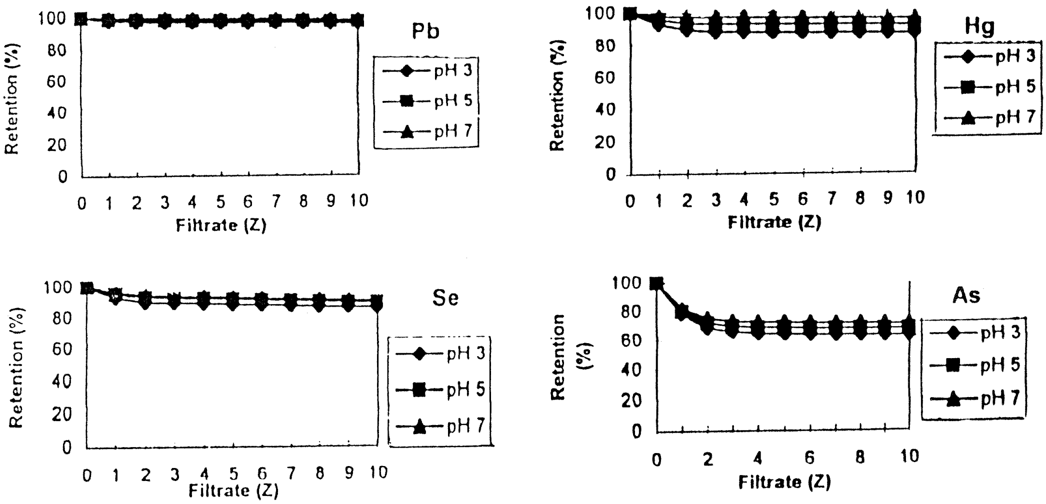

Figure 2. Percentage of retention (%) of Pb(II), Hg(II), As(V), Se(IV) ions by an aqueous solution of poly(maleyl glycine-*co*-acrylamide) at pH 3, 5, and 7.

According to the probable intramolecular complexation of the metal ions by the copolymer, the corresponding parts of the copolymer chains are arranged around the metal ions. This variation of the molecular shape leads to an alteration of the viscosity (21).

As a reference, the copolymer shows a higher viscosity than the homopolymer P(MG) previously reported. This may be attributed primarily to the structural difference introduced for the Am comonomer unit (see Table 2).

The viscosity data demonstrate the role of competing interactions in the formation of intramolecular bonds by virtue of the high content of carboxylic groups in the chain. The intrinsic viscosity of' aqueous solutions (0.1 M NaCl) of the copolymer depends on different pH and at the presence of metal ions Cr(III), Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Hg(II). This was measured at pH 3, 5, and 7 (see Table 3). The intrinsic viscosity in all cases was increased in the presence of the metal ions. At all pH, the viscosity of the copolymer in the presence of the metal ions is generally increased. This behavior can be attributed to a weakening of the intramolecular hydrogen binding attraction forces of the chains, which are caused by an increase of the charges along the macromolecules during the complexation process.

The separation of two metal ions, Hg(II) and Pb(II) and two non-metal ions As(V) and Se(IV) was also studied by LPR method. It was investigated by using a copolymer 2 wt% at pH 3, 5 and 7. As(V) and Se(IV) were retained above 85% and 60% respectively. This retention behavior is almost independent of the pH and only for As(V) it depends lightly of the filtration factor, Z up to achieve a Z = 2.

The intrinsic viscosity decreased in the presence of the inorganic ions. It depends on pH and higher value was found at pH 7. This behavior can be attributed to an intramolecular binding of the chains, caused by As(V) and Se(IV). That corresponds to the fact that non-metal complexation is favored in neutral or alkaline solution. This can also be explained by a higher electron density of the oxygen caused by the positive inductive effect of the As_2O_5 and SeO_2 groups at pH 7 most probably as arsenite and selenite.

Table 2. Intrinsic viscosity [η] of poly(N-maleyl glycine-*co*-acrylamide); P(MG-*co*-Am) at pH 5 (at 35°C, 0.1 M NaCl).

Copolymer	Copolymer composition[a] (F) in MG	Intrinsic viscosity [η] (dL/g)	Molecular mass (Mn) (g/mol)[b]
P(MG-*co*-Am)	0.20	0.450	13.570
	0.40	0.380	13.100
	0.50	0.270	12.500
	0.65	0.150	12.080
	0.69	0.130	11.800
	0.82	0.080	11.200
Homopolymer			
P(MG)		0.056	11.500
P(Am)		0.500	13.800

a) Determined by elemental analyses from N/C ratio

b) Measured at 30°C by vapor pressure osmometry in water

Table 3. Intrinsic viscosity [η] of poly(N-maleyl glycine-*co*-acrylamide)[a]; P(MG-*co*-Am) with inorganic ions at pH 3, 5, and 7 (35°C, 0.1 M NaCl, 20 ppm of metal ions and 40 ppm of non-metal ions)

Copolymer	[η] (dL/g)		
	pH 3	pH 5	pH 7
P(MG-*co*-Am)	0.250	0.270	0.350
P(MG-*co*-Am) complex (eight metal ions)	0.520	0.580	0.601
P(MG-*co*-Am) complex with As(V), Se(IV), Pb(II), and Hg(II)	0.190	0.200	0.220

a) Copolymer composition 1:1, determined by elemental analyses from N/C ratio.

Table 4. Retention percentage of inorganic ions by poly(N-maleyl glycine-*co*-acrylamide); P(MG-*co*-Am) at pH 3, 5 and 7.

Metal Ion	R (%) pH 3	pH 5	pH 7
Pb (II)	85.9	96.9	98.0
Hg (II)	86.9	92.2	96.2
As (V)	63.0	67.8	71.3
Se (IV)	85.0	87.0	93.5

Conclusions

The interaction profiles of poly(N-malcyl glycine-*co*-acrylamide) with eight metal ions have been investigated in aqueous solutions at different pH values. At pH 5 and 7, most metal ions showed retention values > 90% for Zn(II) and Cd(II). At lower pH, the polymer interacted with eight metal ions but only Cr(III), Zn(II), Cd(II), Pb(II) and Cu(II) showed retention values > 90%.

The intrinsic viscosity increased in the presence of metal ions which also depends on pH and the highest value was found at pH 7. This behavior can be attributed to a weakening of the intramolecular hydrogen binding attraction forces of the chains.

Acknowledgments

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