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Interactions of the Water-Soluble Poly(N-Maleyl Glycine-co-Acrylic Acid) as Polychelator with Metal Ions in Aqueous Solution

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NOTES

INTERACTIONS OF THE WATER-SOLUBLE POLY(N-MALEYL GLYCINE-*co*-ACRYLIC ACID) AS POLYCHELATOGEN WITH METAL IONS IN AQUEOUS SOLUTION

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ABSTRACT

The metal complexation of water-soluble poly(N-maleyl glycine-*co*-acrylic acid) with Co(II), Zn(II), Ni(II), Cu(II), Fe(II), Cd(II), Pb(II), and Sr(II) ions was investigated in aqueous phase using the Liquid-Phase Polymer-Based Retention (LPR) technique. The water-soluble P(MG-*co*-AA) copolymer was shown to be useful for the retention of different inorganic ions in conjunction with membrane filtration and their separation from ions not bound to the polymeric reagent. At higher pH, the water-soluble copolymer can

Dedicated to Professor Ernst Bayer on the occasion of his 70th birthday.

be applied to the separation and preconcentration of many metal ions. Maximum capacity values of the copolymer for copper(II) were determined at different pH. Viscometric measurements of the copolymers were performed in the presence of the nine metal ions at different pH values.

INTRODUCTION

Hydrophilic polymers have found great interest as supports for chelating groups [1-6]. Many polymer types have been synthesized by both copolymerization and polymer-analogous reactions [1]. They have been employed for the removal of metal ions from diluted solutions and implicate potential technical application [7-10]. Previously, poly(N-maleyl glycine), PMG, was synthesized and investigated in terms of its complexation properties and applications as polychelators for different metal ions [7].

Recently, the poly(N-maleyl glycine-co-acrylic acid) was also synthesized and characterized [13]. In this paper, the complexing properties of P(MG-co-AA) as polychelator toward nine metal ions are reported. The metal ion binding studies were carried out at different pH and filtration factor using the Liquid-Phase Polymer-Based Retention (LPR) technique.

EXPERIMENTAL

Reagents

Poly(N-maleyl glycine-co-acrylic acid), P(MG-co-AA) was synthesized by radical copolymerization with a 1:1 feed monomer composition in solution using 0.5 mol% of AIBN as the initiator [13]. Prior to the polymer-metal ion interaction studies, the polymer was dissolved in water and purified by membrane filtration using a membrane with a normal 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.

Equipment

The determination of the metal ion concentration was carried out with a Perkin-Elmer 1100 Atomic Absorption Spectrometer. Viscometric measurements were performed with an Ostwald viscometer. For lyophilization, a continuous freeze

dryer (New Brunswick 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 polychelator P(MG-co-AA). Details have been described previously [8-11, 15].

Complexation Procedure

To determine the complex binding capacity, the copolymer (200 mg) was dissolved in water (10 mL). The pH was adjusted by addition of diluted nitric acid or sodium hydroxide solution. The aqueous solutions of the polymer and the metal nitrates or chlorides (2 wt%) 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 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 was stirred for 5 minutes, and then washed with the reservoir fluid at a flow rate of 4-6 ml/min. The filtration fractions ($Z = 1-10$) were collected and the concentration of metal ions in the filtrate and the retentate were determined by atomic absorption spectroscopy. The copolymer was lyophilized for further analytical control.

Maximum Binding Capacity of Copper(II)

For the regeneration of P(MG-co-AA), protolysis was used. The P(MG-co-AA) was saturated with an aqueous solution of copper(II) nitrate (10 wt%). Subsequently, it was washed using the LPR technique. Then the P(MG-co-AA)-copper(II) complex was treated with concentrated nitric acid (100 mg/ml). The concentration of released copper(II) ions was analyzed by absorption atomic spectrometry.

RESULTS AND DISCUSSION

Interactions between the P(MG-co-AA) and nine metal-ions were studied by retention experiments using membrane filtration. This technique allows the investigation of complex formation in homogeneous aqueous phase. Therefore, it is essential for this technique that the molecular mass of the polymer is higher than the nominal exclusion rate of the membrane. Previously it has been shown that the retention percentage of any species bound to the polymer and, therefore, rejected by the membrane of a membrane filtration system can be expressed by the term:

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

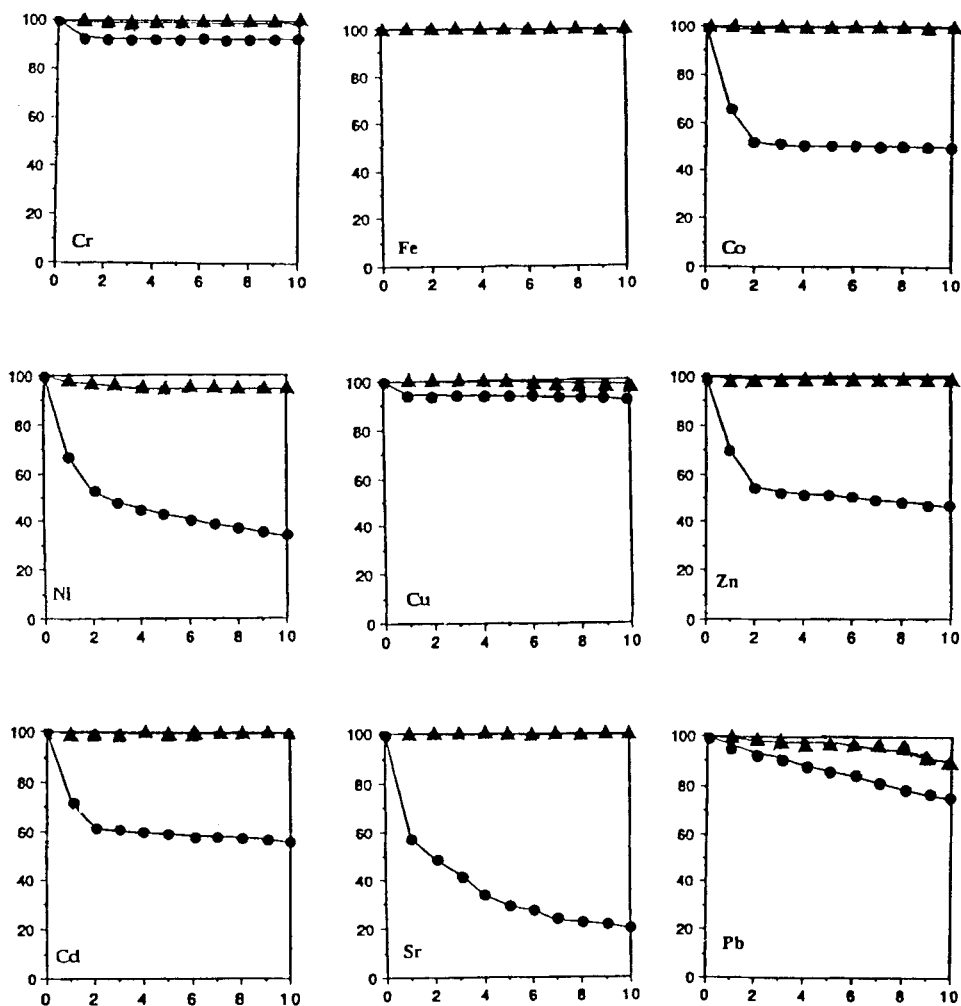


Figure 1. Retention profiles (R%) for different metal ions by an aqueous solution (2 wt%) of P(MG-co-AA) at pH3 (●-) and 5 (-▲-).

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_0 is the initial metal ion concentration in the cell [15-17].

The behavior is documented in retention profiles which are plots of the retention R versus the filtration factor Z , which is defined as the ratio of the volume of filtrate V_f and the volume of cell solution V_0 .

Typical retention profiles of P(MG-co-AA) are shown in Figure 1. In general, only slight complexation with P(MG-co-AA) takes place with all metal

TABLE 1. Retention (%) of Nine Metal Ions by Poly(N-maleyl glycine-co-acrylic Acid)

Metal ion	R(%)	
	pH 3	pH 5
Cr(II)	92.7	99.0
Fe(II)	99.7	99.8
Cd(II)	55.7	99.6
Co(II)	50.0	99.1
Cu(II)	91.6	97.9
Ni(II)	30.6	94.8
Pb(II)	75.3	90.1
Zn(II)	45.5	98.8
Sr(II)	27.6	100.0

ions at pH 3, except for Ni(II), Zn(II) and Sr(II). The Sr(II) ions showed lower interaction tendency than Zn(II), Ni(II) and Cd(II) under these conditions like other metal ions at pH 3. The retention values for Cd(II), Co(II), Ni(II), Zn(II) and Sr(II) are 55.7%, 50.0%, 30.6%, 45.5%, and 27.6%, respectively at $Z = 10$ (see Table 1). A predominant influence of the complexing comonomer units at pH 5 explains the positive interaction with the metal-ions. This binding affinity is valuable for the separation of all metals.

All the other metal ions showed a strong dependence on the pH and filtration factor Z . For example, at pH 5 for a filtration factor of $Z = 10$, Zn(II) showed a retention value of 98.8% and Sr(II) of 100% (see Table 1). At the same pH, the copolymer showed excellent retention for Cu(II), Cd(II), Ni(II), Fe(III), Co(II) and Pb(II). The only representative investigated from the earth alkaline metals Sr(II), was retained, 20.8% at pH 3 and 99.8% at pH 5.

The influence of the solution pH is also illustrated in Figure 1. This factor affects both the complexation reaction and the flow rate through the membrane. In the presence of poly(N-maleyl glycine-co-acrylic acid) P(MG-co-AA), the flow rate in the cell decreased at pH 3 which may be attributed to the interactions of hydrogen bonding between the copolymers and the solvent.

The differences in the complexing ability of the copolymer part on the homopolymer, that was previously reported [8,12], may be attributed primarily to the structural difference in the comonomer repetitive unit. The main reason is that

TABLE 2. Intrinsic Viscosity of Poly(N-maleyl glycine-*co*-acrylic Acid) with Nine Metal Ions at pH 3 and pH 5 (at 35°C, 0.1 M NaCl, 20 ppm of Metal Ions).

Copolymer	$[\eta](\text{dl g}^{-1})$	
	pH = 3	pH = 5
P(MG- <i>co</i> -AA)	0.320	0.350
P(MG- <i>co</i> -M)-M ⁿ⁺ (nine metal ions)	0.507	0.531

TABLE 3. Maximum Binding Capacity of P(MG-*co*-AA) for Cu(II) at Different pH.

pH	Maximum capacity	
	mg/g	mmol/g
1	350	5.6
3	565	8.9
5	777	12.0

the P(MG-*co*-AA) has a structure with three different functional groups, carboxyl and hydroxyl at the side-chain and a tertiary amine in the heterocycle of the polymer which exhibits a relatively strong complexing ability toward metal ions.

On the basis of theoretical studies and the intermolecular metal-crosslinking of macromolecules, Plate et al. [18] were able to predict the principal characteristics of the complex formation between macromolecules and metal ions in relation to the interaction of poly(N-methacryloyl-lysine) with copper(II) ions.

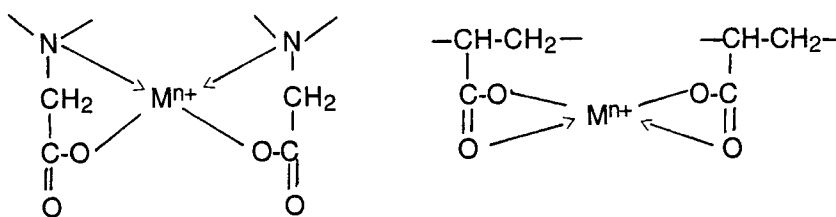
Depending on the pH of the medium, polyelectrolytes are capable to form several types of complexes with the participation of carboxyl, hydroxyl or amino-groups.

According to the probable intramolecular complexation of the metal ions by the copolymer, the corresponding moieties of the copolymer chains are arranged around the metal ions. This variation of the molecular shape leads to an alteration of the viscosity [19].

The intrinsic viscosity of aqueous solutions (0.1 M NaCl) of the copolymer depends on the pH and of the presence of metal ions Cr(III), Fe(III), Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Sr(II), (see Table 2). At both pH it is increased in the presence of the metal ions. 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 maximum binding capacity of the polychelatogen was also investigated for copper(u). The P(MG-co-AA) binds 5.6-12.0 mmol metal/g polymer depending on the pH (see Table 3). Maximum capacity test with complete saturation of the chelating copolymer with Cu(II) proved the insolubility of the copolymer chelate formed with occurring precipitation.

Accordingly, poly(N-maleyl glycine-co-acrylic acid) forms from the two comonomer moieties via the following intramolecular metal cross-linking reactions:



As a reference, the copolymer showed a higher viscosity and maximum capacity than the homopolymer [8, 12]. This may be attributed primarily to the effect of the acrylic acid moiety.

CONCLUSIONS

Hydrophilic copolymer containing chains with carboxyl, hydroxyl and possible amino ligands were found to interact with all the metal ions investigated at pH 5 forming soluble copolymer metal complexes.

The interaction profiles of aqueous solutions of poly(N-maleyl glycine-co-acrylic acid) with nine metal ions have been investigated at different pH values. At pH 5, most metal ions showed retention values > 90%. At pH 3, the polymer interacts with all of the nine metal ions but only Cr(III), Fe(III) and Cu(II) showed retention values > 90%.

The intrinsic viscosity increased in the presence of the metal ions (pH 5) and it depends also on the pH, showing higher values at pH 5 than at pH 3.

The maximum capacity of P(MG-co-AA) with copper(II) ions showed a strong dependence on the pH with a maximum value of 777 mg copper(II)/g of copolymer.

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